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LITHIUM INORGANIC ELECTROLYTE BATTERY DEVELOPMENT.(U)
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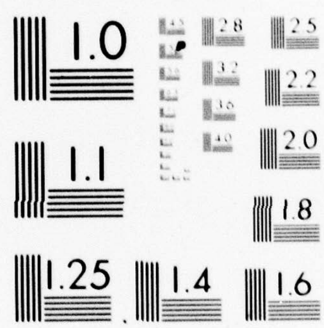

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AFAPL-TR-79-2026

# LITHIUM INORGANIC ELECTROLYTE BATTERY DEVELOPMENT



GTE SYLVANIA INCORPORATED
ELECTRONIC SYSTEMS GROUP
COMMUNICATION SYSTEMS DIVISION
189 B STREET
NEEDHAM HEIGHTS, MA 02194

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AIR FORCE AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

## NOTICE



This technical report has been reviewed and is approved for publication.

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**20. ABSTRACT (Continue on reverse side if necessary and identify by block number)**

This report presents the results of the first half of a three-year program to conduct exploratory development to improve the safety/performance characteristics of lithium anode/inorganic electrolyte batteries. Development has been conducted in 3 major areas: capacity retention of cylindrical cells, low temperature capability of cylindrical cells, and abuse tests of cylindrical and prismatic cells. Significant accomplishments include providing capacity down to the 3.0 volt level cutoff at -40 degrees and no

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venting or explosion of cells during abuse tests, except during incineration when it is expected.

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## SECTION I

## INTRODUCTION

The objective of this program is to provide safe and reliable lithium inorganic electrolyte primary battery technology which meets the performance requirements of Air Force applications. The specific items to be investigated are:

1) Establish storage degradation rates for cells in which the anode capacity limits cell capacity and compare this data with that of cells in which the cathode capacity limits the cell capacity.
2) Establish the conditions, parameters, and ranges of parameters under which cell overheating, venting, and/or explosions occur.
3) Determine the cause of the abnormal cell operation investigated in 2. above.
4) Eliminate or control the cause of abnormal cell operation to a level where conditions of hazardous/unsafe operation cannot develop.
5) Improve the low temperature performance until at least 25 percent of room temperature capacity (25°C) is available at -40°C.
6) Eliminate or reduce passivation effects after extended storage to an acceptable level for use in life support equipment, missile silo, and spacecraft applications.
7) Establish the suitability of lithium-sulfuryl chloride batteries for life support, missile silo and spacecraft applications.
8) Establish techniques for safely inerting and disposing of lithium inorganic electrolyte batteries that are consistent with possible future materials reclamation.

The above items are prepared in three major sections consisting of:

1) Capacity retention of cylindrical cells
2) Low temperature tests of cylindrical cells
3) Abuse tests of cylindrical and prismatic cells.

## SECTION II

## CAPACITY RETENTION

1. PASSIVATION TEST

a. Purpose

The purpose of this test is to gather data for several cell designs to assist in the establishment of techniques and designs which will optimize cell performance.

b. General

A passivating film of lithium chloride is formed on the anode surface of lithium thionyl chloride cells, and on lithium sulfuryl chloride cells, as a result of the interaction between the lithium and the electrolyte. This film can cause a significant output voltage drop at the beginning of a high-rate discharge following a period of inactive storage. As the discharge continues, the anode surface is stripped of the passivating film and the voltage drop decreases. The magnitude of the voltage drop and the recovery rate are functions of the applied discharge rate for each combination of storage time, storage temperature, and cell chemical and physical design.

c. Test Data

Table 1 illustrates the results from the passivation test conducted at room temperature. After one month storage, the voltage delays at the start of discharge fell into two groups. The $SOCl_2$ + Ca and $SOCl_2$ electrolyte types had voltage delays of 6 seconds or less. The other two electrolyte types had voltage delays significantly greater. After a two-month storage duration, all four types of electrolyte had voltage delays approximately one hour or greater. The $SO_2Cl_2$ and $SO_2Cl_2$+Ca types of electrolyte were not available until recently, and they will be tested in the Technical Replan Program, which will repeat all of the passivation test. The electrolytes will be of better quality as far as hydrolysis products are concerned, and a more efficient filling system will be used. The preliminary indication from these tests, as confirmed by the low temperature tests, is that $SOCl_2$ electrolyte performs better than the other types of electrolyte tested.

TABLE 1

PASSIVATION TESTS (3.0 VOLT CUT-OFF)

| Electrolyte Type | Baseline Capacity Delay | | Month 1 Capacity Delay | | Month 2 Capacity Delay | |
|---|---|---|---|---|---|---|
| $SOCl_2$ | 5.112Ah | | 3.981 Ah | .2 sec. | 4.472Ah | 1.8hrs |
| | 5.182Ah | | 4.928 Ah | .8 sec. | 1.821Ah | 2.0hrs |
| | 5.012Ah | | 4.218 Ah | 1.2 sec. | 3.157Ah | 2.0hrs |
| $SOCl_2 + SO_2$ | 5.151Ah | | 5.066Ah | 2hr1min11sec | 4.750Ah | 2.0hrs |
| | 5.054Ah | | 4.600Ah | 2hr16m 45sec | 4.768Ah | 2.0hrs |
| | 5.172Ah | | 5.117Ah | 19m 20sec | 4.143Ah | 1.6hrs |
| $SOCl_2$ + Ca | 5.132Ah | .31 sec. | 4.055Ah | 0 sec. | 2.17Ah | 2 hrs |
| | 4.949Ah | .37 sec. | 4.025Ah | 6 sec. | 1.90Ah | 56min10sec |
| | 5.009Ah | .50 sec. | 4.616Ah | 0 sec. | 2.18An | 50min51sec |
| $SO_2Cl_2$ | 4.8Ah | | 1.98Ah | 1 min 29 sec | 4.10Ah | - |
| | 4.9Ah | | 2.10Ah | 29 sec | 4.35Ah | - |
| | 4.6Ah | | 2.00Ah | 34 sec | 4.52Ah | - |

NOTES:
1. Capacity in ampere-hours
2. Test Article Size - D cell
3. Stored at 55°C
4. Current density during voltage delay of 2 $mA/cm^2$ and during discharge of 1 $mA/cm^2$.

2. STORAGE DEGRADATION

a. Purpose

The purpose of this test is to gather data for determining the effects of long-term storage degradation on two DD cell configurations (cathode-limited and lithium-limited design).

b. Baseline Capacity of DD Cells

Twenty lithium-limited (L/L) cells and 20 cathode-limited (C/L) cells were filled with standard $SOCl_2$ electrolyte. These cells were discharged at a rate of 1 $mA/cm^2$ (88 mA) in order to establish a baseline capacity. A baseline capacity is considered to be the ampere-hours obtained from a cell that is discharged immediately after manufacturing.

The baseline ampere-hour capacity established for a lithium-limited cell is 9.42 ampere-hours at a cutoff voltage of 3.0 volts.

The baseline ampere-hour capacity established for cathode-limited cells is 28.68 ampere-hours at a cutoff voltage of 3.0 volts.

c. Storage Cells Data

Over an eight-month duration, the data for percentage of ampere-hour capacity with respect to the baseline is inconsistent. For example, the cathode-limited storage cells from +25°C storage for four months had a 2.7 percent higher ampere-hour capacity than those from two months, and the eight-month cells were 11.2 percent better than six-month cells. The cells from +55°C showed even more inconsistency in capacity. At +25°C, the lithium-limited cells reacted with a more persistent loss of capacity; however, the loss over eight months was 6 percent of baseline capacity, and this is a greater loss than should be expected. Table 2 illustrates this data.

TABLE 2

STORAGE DEGRADATION

| LITHIUM-LIMITED @ 25°C AMP-HR CAPACITY | | LITHIUM-LIMITED @ 55°C AMP-HR CAPACITY | |
|---|---|---|---|
| Baseline | 9.42Ah 100% | Baseline | 9.42Ah 100% |
| Two-Month | 9.41Ah or 99.9% | Two-Month | 6.18Ah or 65.6% |
| Four-Month | 9.25Ah or 98.1% | Four-Month | 6.66Ah or 70.7% |
| Six-Month | 9.00Ah or 95.5% | Six-Month | 4.57Ah or 49.0% |
| Eight-Month | 8.68Ah or 94.0% | | |
| **CATHODE LIMITED @ 25°C AMP-HR CAPACITY** | | **CATHODE LIMITED @ 55°C AMP-HR CAPACITY** | |
| Baseline | 28.68Ah 100% | Baseline | 28.68 100% |
| Two-Month | 27.90Ah or 97.3% | Two-Month | 14.46Ah or 50.4% |
| Four-Month | 28.90Ah or 100.0% | Four-Month | 2.16Ah or 7.5% |
| Six-Month | 24.80Ah or 86.5% | Six-Month | 4.62Ah or 16.1% |
| Eight-Month | 28.00Ah or 97.7% | | |

After removing several cells from storage and performing an analysis of hydrolysis products, it was revealed that the water concentration was 570 PPM. This concentration increases the degradation rate; consequently, inconsistent data were produced. Because of the above, testing of cells was discontinued from $+55^{o}C$ storage after the six-month test was completed.

The cells from $+25^{o}C$ storage, which continually give a high ampere-hour capacity, are still being tested.

3. LITHIUM ANALYSIS

a. General

As part of our investigations, one fresh and one discharged cell from each group tested is disassembled to determine the percentage of lithium remaining. A titration method is used to analyze remaining lithium. An analysis procedure is included as part of this report, which will explain what adverse effect could arise when the titration is not performed correctly. All future analyses to determine remaining lithium will be conducted in our newly constructed chemical laboratory. The enclosed table indicates that, in most cells, the lithium found by analysis is in agreement with the starting quantity built into the cell as well as the amount which should be remaining after discharge.

We feel several of the unexpected results are due to procedural error. For example, there were several cells that indicated a loss of nearly 3 grams of lithium while in storage with no load being applied. Known factors that could contribute to such results are procedural error where electrolyte remains in the cell to react with water to form HCl and $H_2SO_3$ (which neutralizes some of the LiOH prior to titration), and an internal short. If there had been an internal short, the open circuit voltage, which was monitored prior to analysis, would have been lower than it was. Due to the probability of procedural error, which will be corrected in the new laboratory, it is considered that conclusions cannot be made with any degree of reasonable assurance.

b. Determination of Lithium by Titration

The purpose of the titration is to determine the amount of lithium remaining in the cell prior to or after discharge.

The cell is disassembled and the cathode and electrolyte are removed. The lithium which remains in the cell is washed with tetrahydrofuran (THF) to remove any electrolyte that still remains. The lithium is removed in small quantities from the cell and reacted with water to obtain a lithium hydroxide solution, which is then titrated against a standard solution of hydrochloric acid (HCl).

A standard solution of 0.1 N HCl is used for the titration with Bromothymol blue (0.04%) as an indicator. The HCl is then titrated until the characteristic yellow color is observed signaling the end point.

c. <u>Titration Data Table Description</u>

To assist in the understanding of Table 3, its terminology is listed below:

(1) D L/L - The cell is a single D size, lithium-limited.

(2) D C/L - The cell is a single D size, cathode-limited.

(3) DD L/L - The cell is a double D, lithium-limited.

(4) DD C/L - The cell is a double D, cathode-limited.

(5) Baseline - The cell is discharged shortly after manufacture and activation.

(6) Storage Degradation Cells - The cells are stored for a specified time at a specified temperature prior to discharge.

(7) Pre-Discharge - The cells are analyzed for lithium amount remaining when removed from storage prior to any discharge.

(8) Post-Discharge - The cells are analyzed for remaining lithium after they have been discharged to 3.0 volts.

(9) Grams of Lithium - This column indicates the amount of lithium used to manufacture the cell as well as the amount of lithium remaining prior to or after discharge as determined by titration.

(10) Theoretical Capacity - The theoretical capacity is based on receiving 3.89 ampere-hours per each gram of lithium; therefore, a D L/L cell which used 1.42 grams of lithium has a theoretical ampere-hour of 5.52 ampere-hours.

TABLE 3

TITRATION DATA

| ELECTROLYTE | CELL TYPE | TEST CONDITION | GRAMS OF LITHIUM WHEN MANUFACTURED | GRAMS OF LITHIUM AFTER ANALYSIS | AMP HOURS @ 3.0 VOLTS | % OF LITHIUM UTILIZED | % OF THEORETICAL CAPACITY |
|---|---|---|---|---|---|---|---|
| $SOCl_2$ | D L/L | BASELINE | 1.42 | 0.027 | 5.012 | 98% | 90% |
| $SOCl_2$+Ca | D L/L | BASELINE | 1.42 | 0.0 | 5.132 | 100% | 92% |
| $SO_2Cl_2$ | D L/L | BASELINE | 1.42 | 0.016 | 4.676 | 99% | 80% |
| $SOCl_2$+$SO_2$ | D L/L | 1 month storage @ +55°C | 1.42 | 0.158 | 5.066 | 89% | 91% |
| $SOCl_2$ | D L/L | 2 month storage @ +55°C | 1.42 | 0.0 | 3.157 | 100% | 57% |
| $SOCl_2$ | DD L/L | BASELINE | 2.72 | 0.0 | 9.435 | 100% | 89% |
| | DD C/L | | 8.1 | 0.625 | 25.100 | 92% | 80% |
| | DD C/L | | 8.1 | 0.282 | 29.840 | 97% | 95% |
| | | Storage Degradation Cells Listed Below | | | | | |
| $SOCl_2$ | DD L/L | 2 mo. @ +25°C Pre-Discharge | 2.72 | 2.72 | | 0.0% | |
| | DD L/L | 2 mo @ +55°C Pre-Discharge | 2.72 | 2.68 | | 0.001% | |
| | DD L/L | 4 mo. @ +25°C Pre-Discharge | 2.72 | 1.10 | | 60% | |
| | DD L/L | 4 mo. @ +55°C Pre-Discharge | 2.72 | 1.15 | | 58% | |
| | DD C/L | 2 mo. @ +25°C Pre-Discharge | 8.1 | 7.76 | | 0.04% | |
| | DD C/L | 2 mo. @ +55°C Pre-Discharge | 8.1 | 7.46 | | 0.01% | |
| | DD C/L | 4 mo. @ +25°C Pre-Discharge | 8.1 | 5.13 | | 37% | |
| | DD C/L | 4 mo. @ +55°C Pre-Discharge | 8.1 | 5.11 | | 37% | |
| | DD L/L | 2 mo. @ +25°C Post-Discharge | 2.72 | 0.01 | 9.58 | 99% | 91% |
| | DD L/L | 2 mo. @ +55°C Post-Discharge | 2.72 | 0.78 | 5.68 | 71% | 54% |
| | DD C/L | 2 mo. @ +25°C Post-Discharge | 8.1 | 0.18 | 27.69 | 93% | 88% |
| | DD C/L | 2 mo. @ +55°C Post-Discharge | 8.1 | 0.28 | 23.48 | 96% | 90% |
| | DD C/L | 4 mo. @ +25°C Post-Discharge | 8.1 | 0.65 | 29.70 | 92% | 94% |
| | DD C/L | 4 mo. @ +55°C Post-Discharge | 8.1 | 4.79 | 2.15 | 40% | 7% |
| | DD C/L | 6 mo. @ +55°C Pre-Discharge | 8.1 | 5.15 | | 36% | |
| $SOCl_2$ | DD C/L | 6 mo. @ +55°C Post-Discharge | 8.1 | 2.16 | 9.96 | 73% | 32% |

## 4. ANALYSIS OF HYDROLYSIS PRODUCTS

The DD cells, built last year and stored without electrolyte, were tested to prove their acceptability for downstream testing programs. They appeared to be satisfactory when opened and visually inspected. However, the absence of dark spots on the anodes is no proof that the carbon is not wet, since carbon does not give off water at room temperature.

Nine cells were filled with electrolyte of known water concentration. After three days, three cells were opened and analyzed for hydrolysis products using IR. After two more days (a total of five days) two more cells were opened and analyzed in the same manner. Finally, after five more days (a total of ten days), the remaining three cells were opened and analyzed.

The results (see Table 4) show that the content of hydrolysis products in the electrolyte remains without significant change after three days and throughout the experiment.

TABLE 4

HYDROLYSIS RESULTS

| TIME ELAPSED PRIOR TO ANALYSIS | 3 DAYS / 3 CELLS | 5 DAYS / 3 CELLS | 10 DAYS / 3 CELLS |
|---|---|---|---|
| Average $H_2O$ content | 67 PPM | 68 PPM | 58 PPM |
| Total Average of Test | | $H_2O$ = 64 PPM | |

It has been concluded that the carbon does not contribute significantly to hydrolysis products in the electrolyte. Therefore, it has been decided that these cells can be used in the continuing test program.

A summary of the analysis of hydrolysis products is as follows. Nine dry cells were removed from storage within the dry room and filled with dry electrolyte (less than 20 PPM). Three sets of three cells each had their electrolyte removed and analyzed for the amount of water absorbed by the carbon and separator paper during dry storage. The water level of the cells tested was considered to be low; therefore, the dry cells in storage are recommended for use.

## SECTION III

## LOW TEMPERATURE

1. LOW TEMPERATURE TESTS

   a. Purpose

The purpose of this test is to gather sufficient data of two cell designs at several temperatures to assist in the establishment of techniques and designs to optimize cell ampere-hour capacity.

   b. General

The electrolyte conductivity of lithium thionyl chloride and lithium sulfuryl chloride cells decreases with a decrease in temperature. This is expected to cause a substantial reduction of cell output capacity when operated at normal discharge rates at low temperatures. This report will update all available data on the cell performance of wound D cells tested at +25$^{o}$C, -20$^{o}$C, and -40$^{o}$C.

   c. Low Temperature Test Data

Table 5 shows the wound cells ampere-hour capacities achieved. Due to procedural error, the cutoff voltages were not kept consistently at 2.0 volts. Therefore, comparisons to room temperature capacities are difficult to make. However, it appears from the results that $SOCl_2$ performs much better at low temperatures than $SO_2Cl_2$.

2. HALF "C" WOUND CELLS

A series of wound cells of 1/2 "C" size was built and tested at room temperature (25$^{o}$C) and at -40$^{o}$C with the purpose of establishing the capability of the lithium thionyl chloride battery system to operate at this low temperature. The 1/2 "C" cell in wound electrode configuration was selected as a test vehicle, since it was suggested as a likely candidate for use in the manpack radio. The test results obtained so far are summarized in Table 6, while the individual discharge curves are included in Figures 1 through 8.

The performance of these cells at room temperature appears quite satisfactory, both at 1 mA/cm$^2$ and 3 mA/cm$^2$. The full capacity of these cells is realized only by extending the discharge to 2.0 V although with the exception of one cell, the discharge of 3.0V cutoff line resulted in as

## TABLE 5

### LOW TEMPERATURE TEST DATA

| ITEM NO. | CELL TYPE | SERIAL NO. | ELECTROLYTE TYPE | DISCHARGE TEMPERATURE | AMP-HOUR CAPACITY | CUTOFF VOLTAGE |
|---|---|---|---|---|---|---|
| 1 | D3 | 12 | $SOCl_2$ | +25°C | 10.77 | 2.0 |
| 2 | | 13 | | | 10.51 | |
| 3 | | 14 | | | 11.51 | |
| 4 | | 15 | | | 12.13 | |
| 5 | | 16 | | +25°C | 11.51 | 2.0 |
| 6 | | 7 | | -20°C | 7.229 | 2.0 |
| 7 | | 8 | | | 7.259 | |
| 8 | | 9 | | | 7.257 | |
| 9 | | 10 | | | 7.501 | |
| 10 | | 11 | | -20°C | 7.106 | 2.0 |
| 11 | | 1 | | -40°C | 2.933 | 2.8 |
| 12 | | 3 | | | 4.212 | 2.4 |
| 13 | | 4 | | | 3.302 | 2.7 |
| 14 | | 5 | | | 2.833 | 2.8 |
| 15 | | 6 | | | 3.253 | 2.8 |
| 16 | | 18 | | | 5.042 | 2.0 |
| 17 | | 19 | $SOCl_2$ | -40°C | 5.147 | 2.0 |
| 18 | | | $SO_2Cl_2$ | +25°C | 12.41 | 3.0 |
| 19 | | | | | 11.84 | |
| 20 | | | | | 11.68 | |
| 21 | | | | | 10.06 | |
| 22 | | | | +25°C | 12.90 | |
| 23 | | | | -40°C | 0 | |
| 24 | | | | | 0 | |
| 25 | | | | | 0 | |
| 26 | | | | | 0 | |
| 27 | | | | -40°C | 0 | |
| 28 | | | | -20°C | 2.10 | |
| 29 | | | | | 1.86 | |
| 30 | | | | | 1.30 | |
| 31 | | | | | 1.35 | |
| 32 | D3 | | $SO_2Cl_2$ | -20°C | 2.41 | 3.0 |

## TABLE 6

### HALF "C" WOUND CELL TEST RESULTS

| TEMPERATURE °C | CURRENT DENSITY $mA/cm^2$ | DISCHARGE CAPACITY (AH) to a voltage cutoff line of 3.0 | 2.0 | 1.0 | TEST NO. |
|---|---|---|---|---|---|
| 25 | 1 | 1.91 | 2.10 | - | 1 |
| | | 1.97 | 2.10 | - | 2 |
| | 3 | 1.46 | 1.70 | - | 3 |
| | | 1.86 | 1.97 | - | 4 |
| -40 | 1 | 0.7 | 0.96 | 1.00 | 5 |
| | | 0.0 | 0.94 | 1.27 | 6 |
| | 3 | 0.0 | 0.164 | 1.0 | 7 |
| | | 0.0 | 0.308 | 0.79 | 8 |

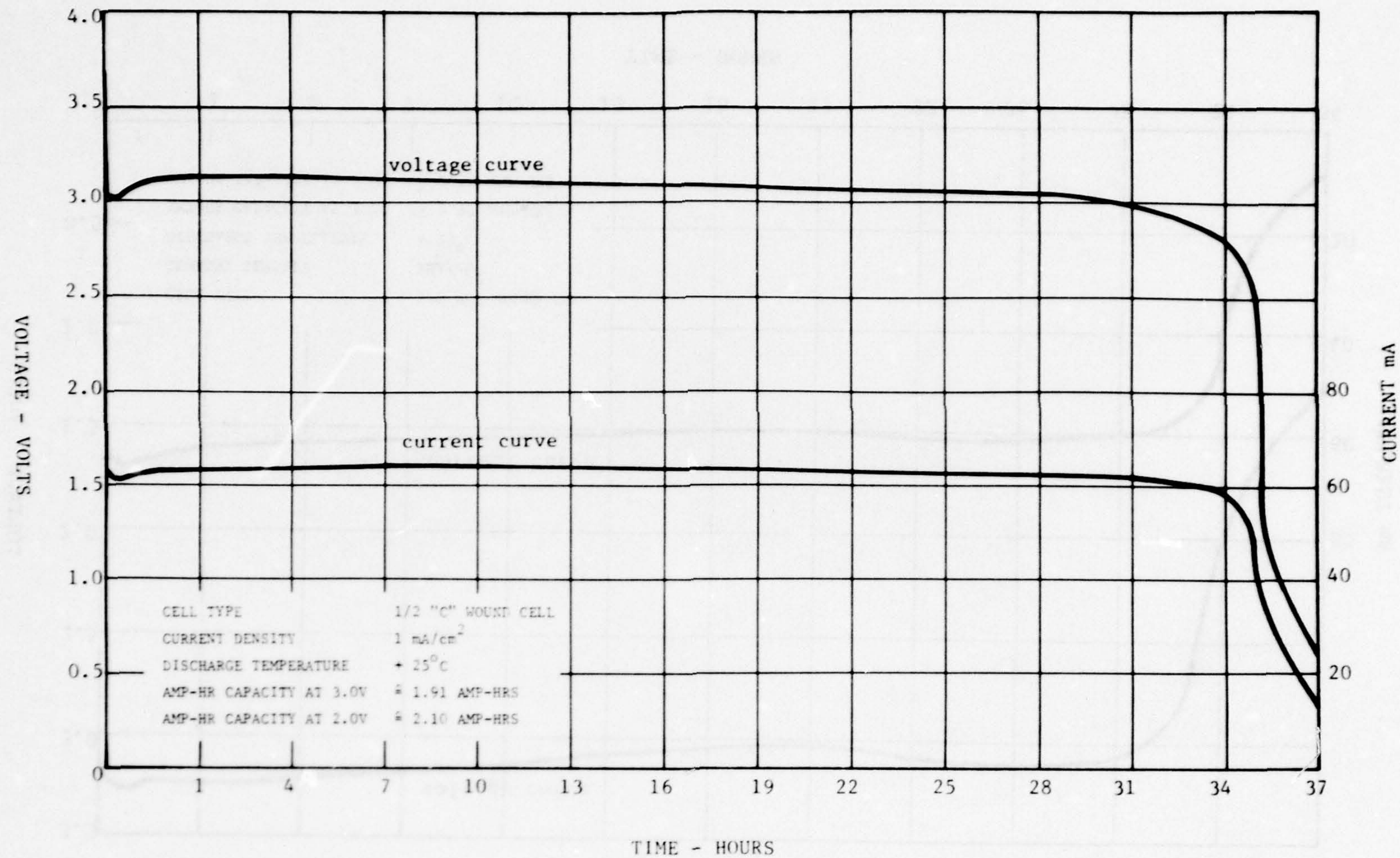


Figure 1. Discharge Curves - Low Temperature Test 1

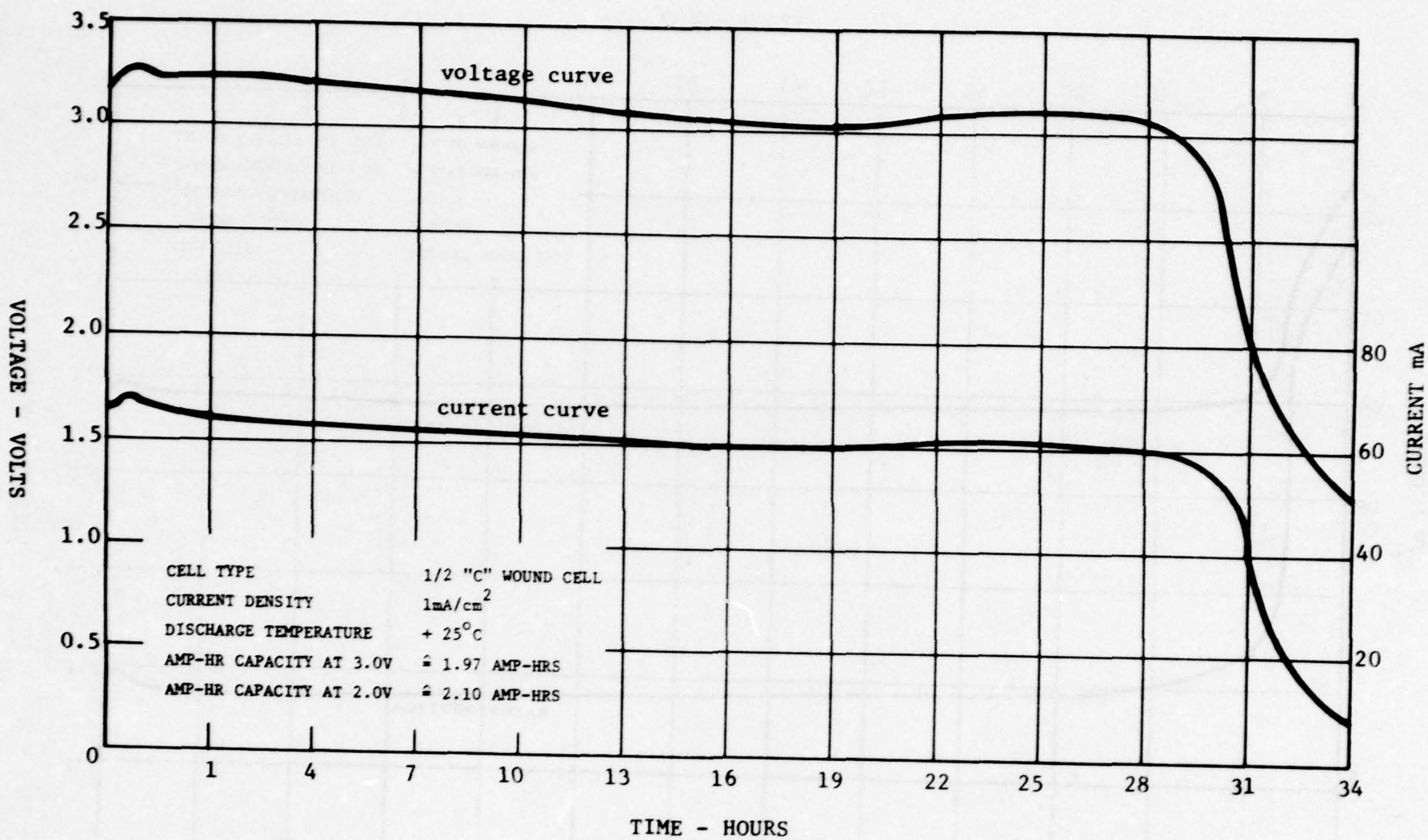


Figure 2. Discharge Curves - Low Temperature Test 2

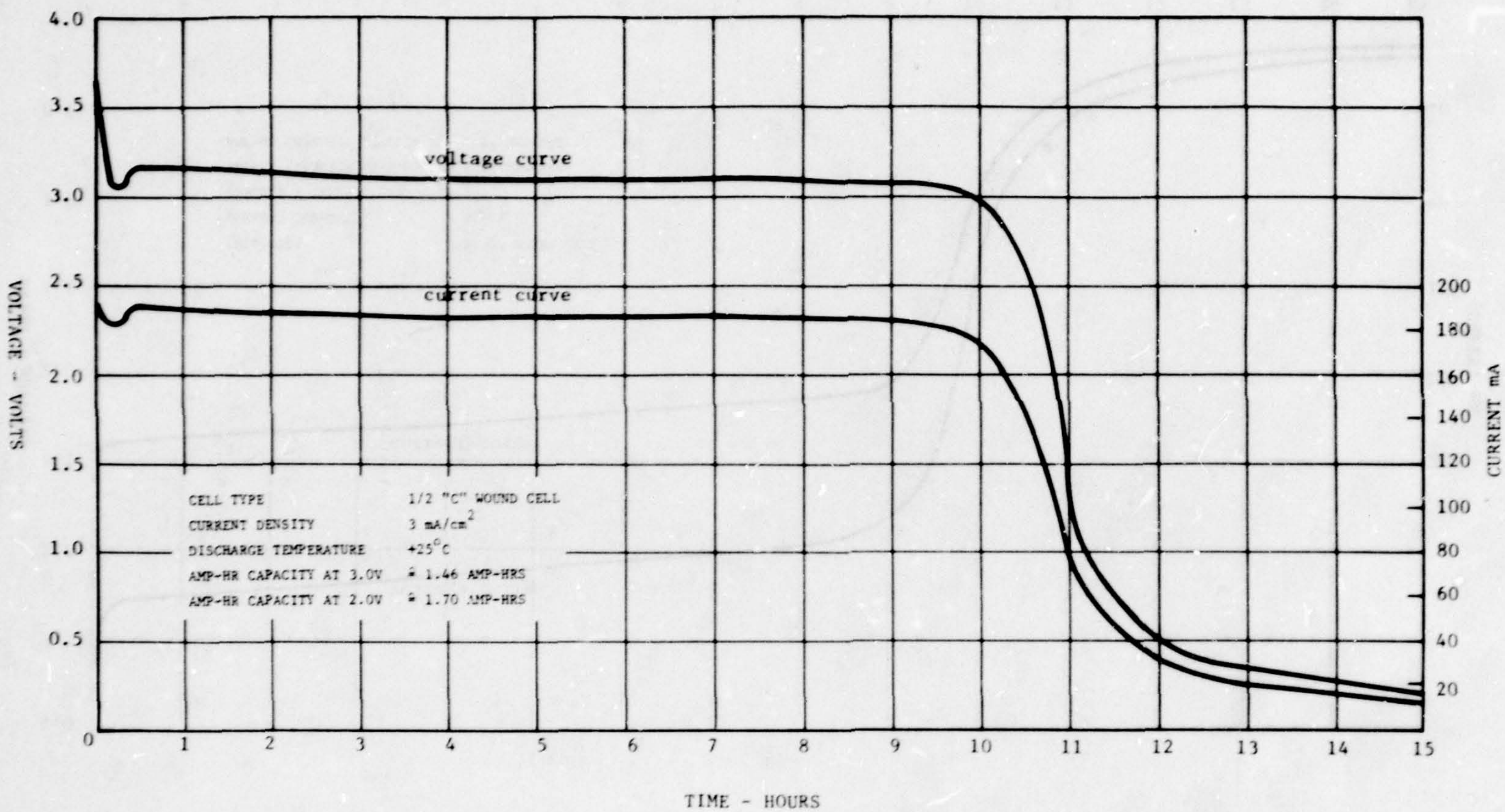


Figure 3. Discharge Curves - Low Temperature Test 3

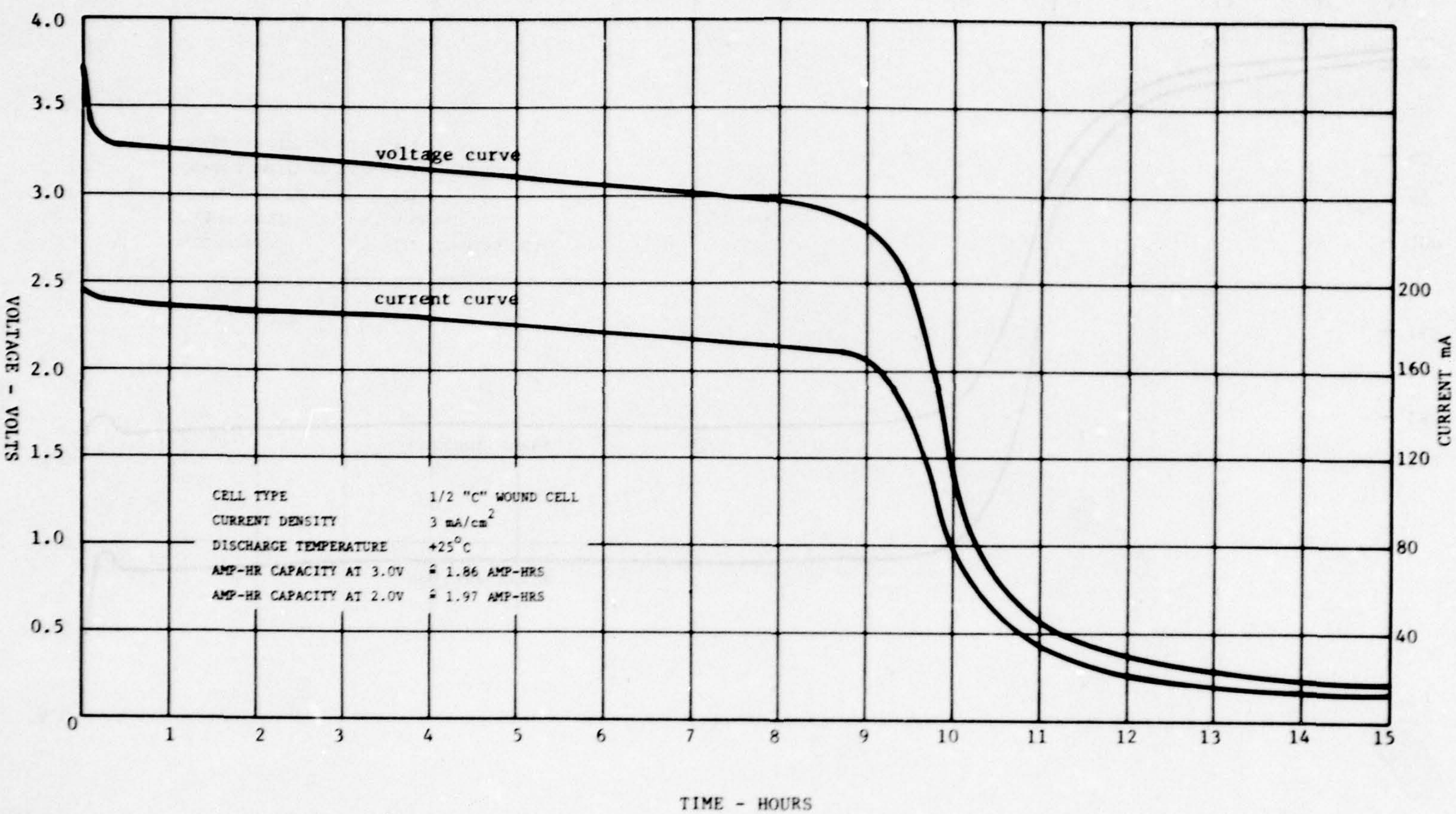


Figure 4. Discharge Curves - Low Temperature Test 4

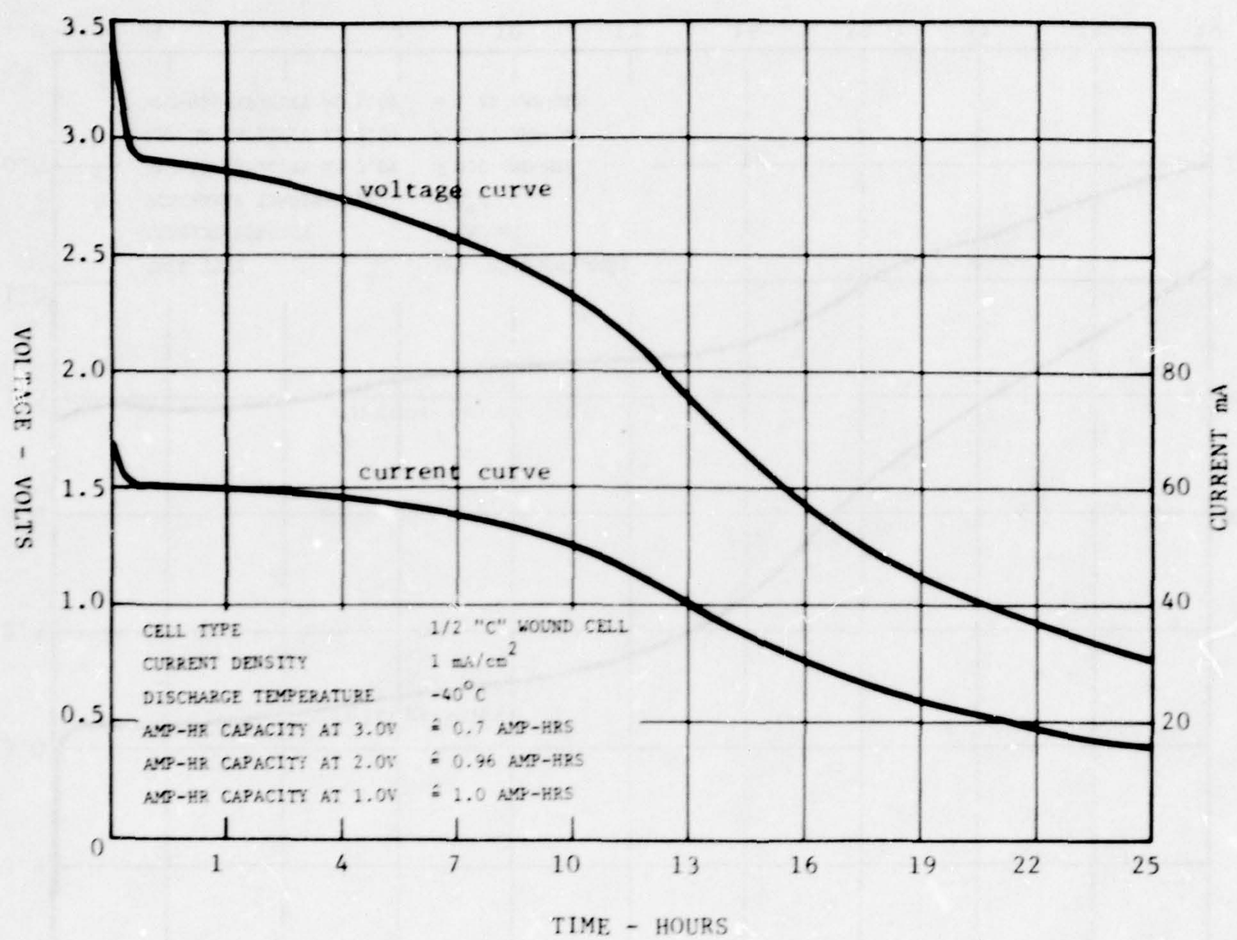


Figure 5. Discharge Curves - Low Temperature Test 5

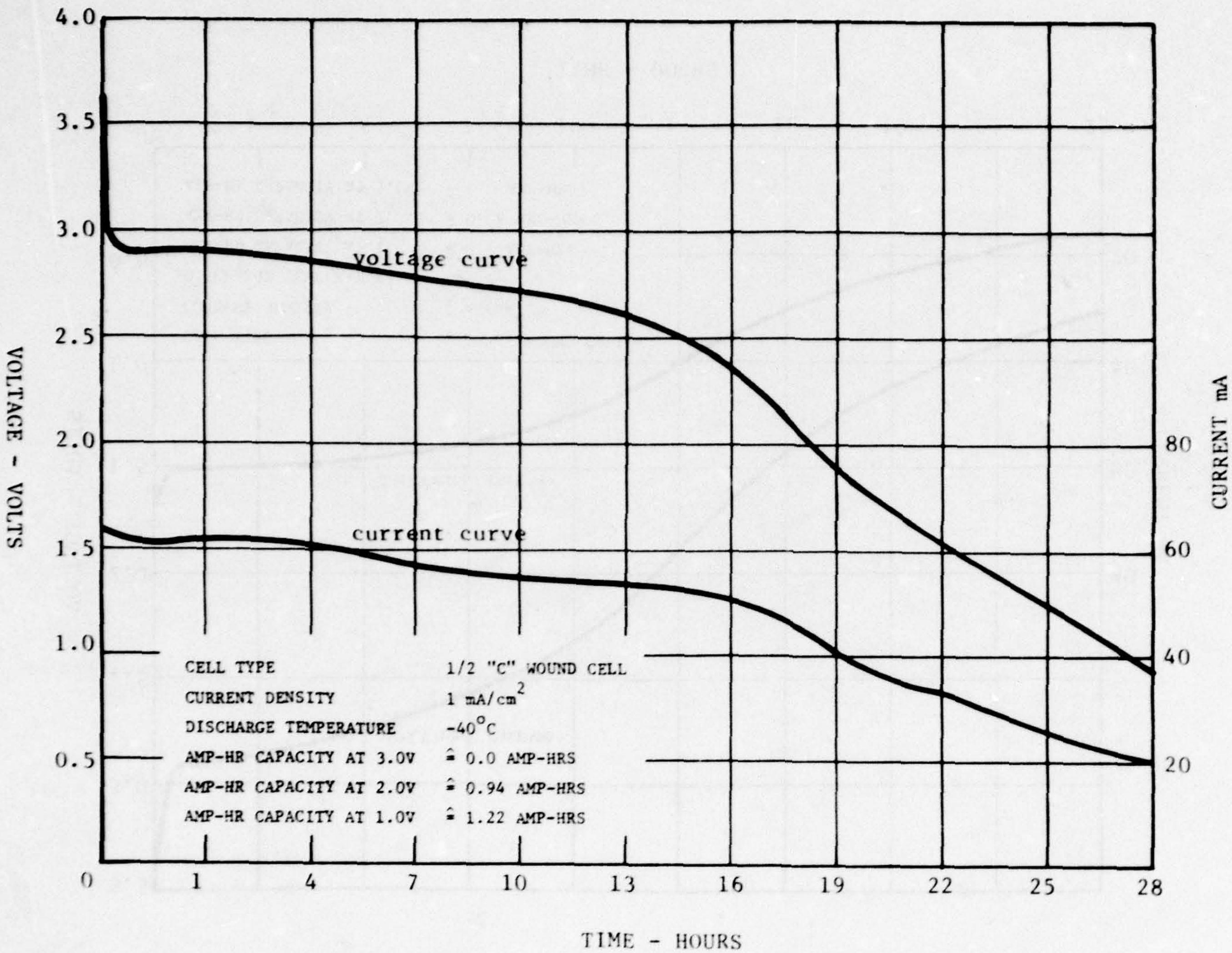


Figure 6. Discharge Curves - Low Temperature Test 6

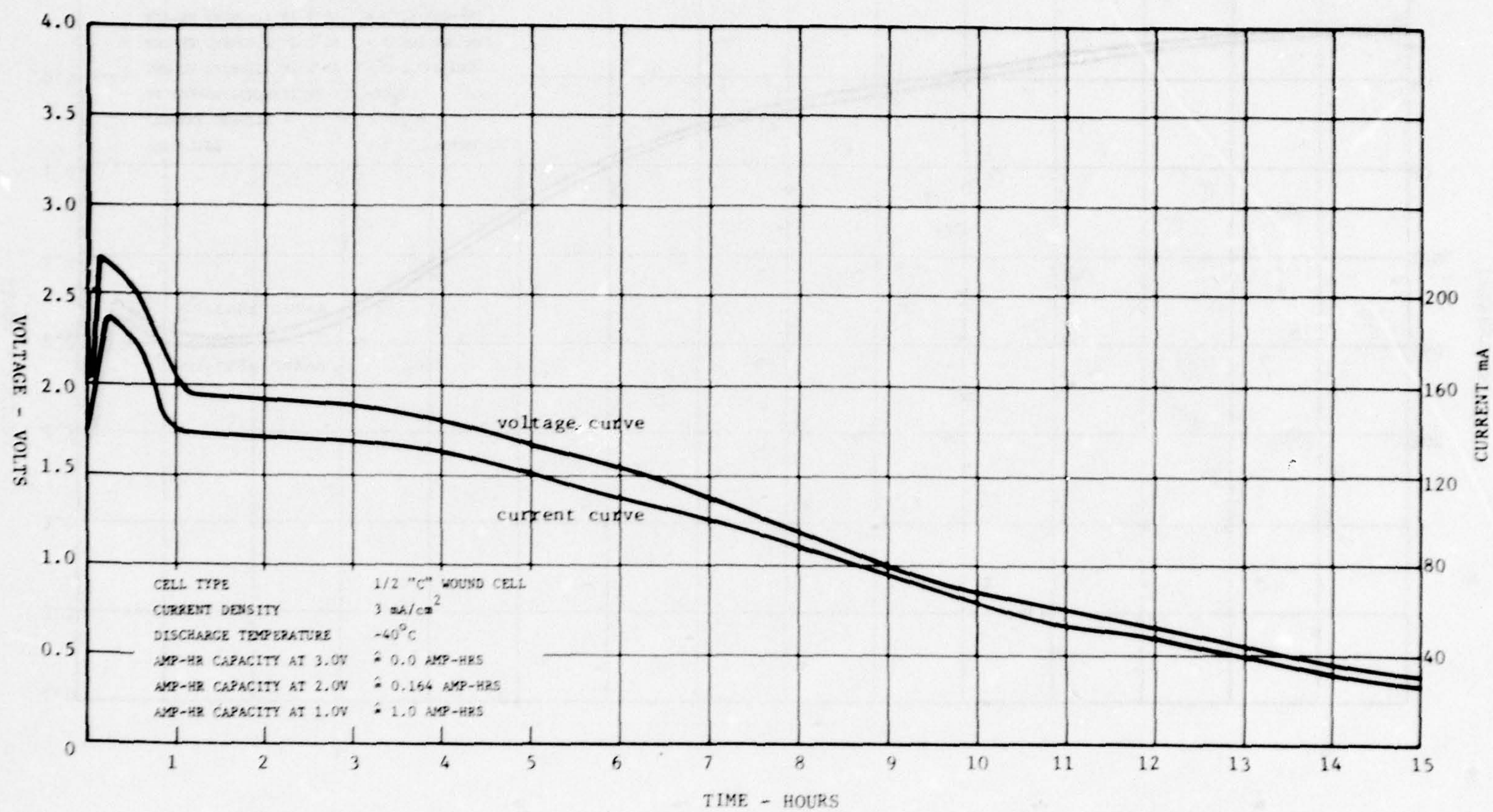


Figure 7. Discharge Curves - Low Temperature Test 7

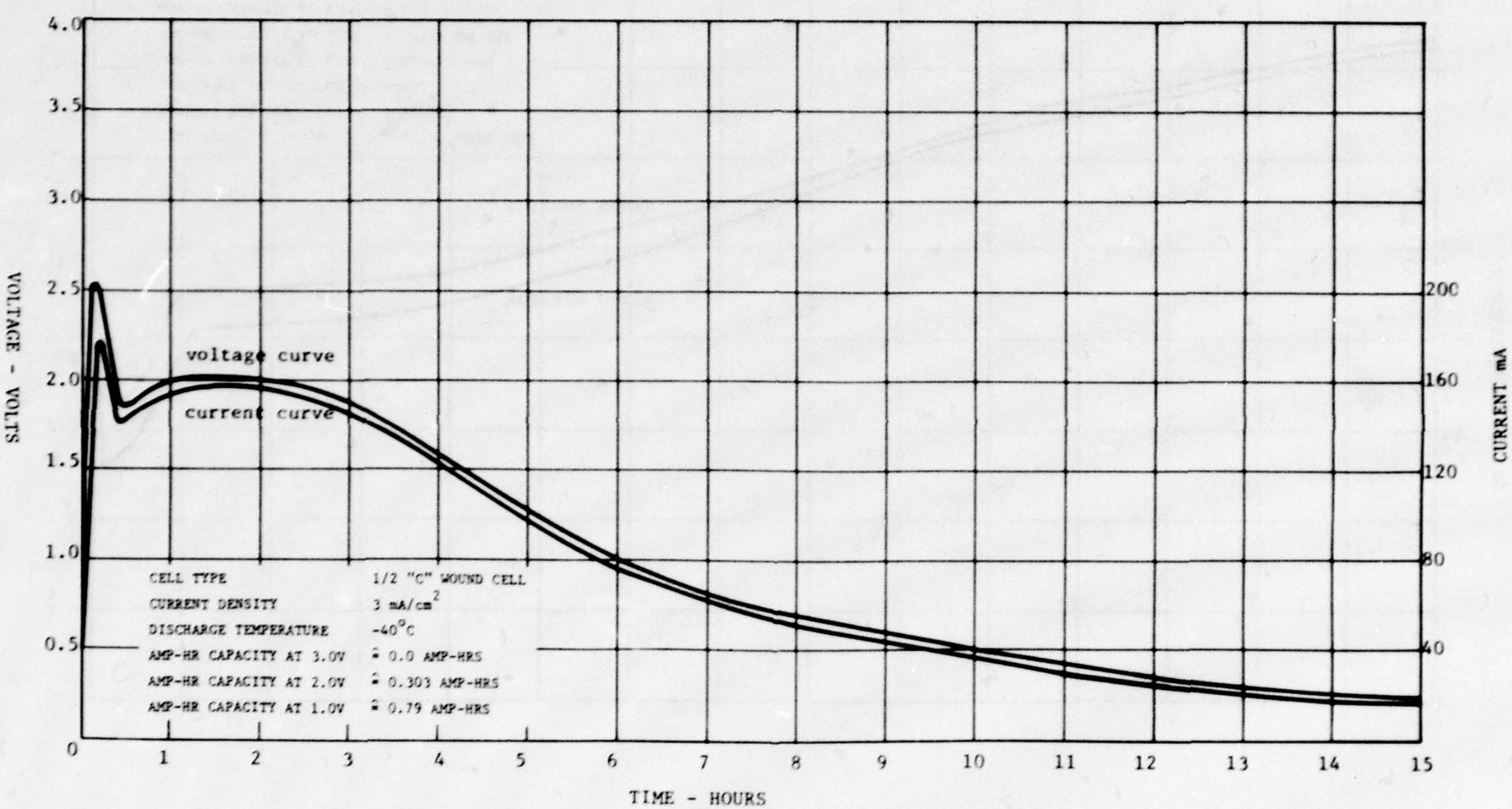


Figure 8. Discharge Curves - Low Temperature Test 8

high a capacity as could be expected. The maximum energy density realized at room temperature was 229.5 Wh/kg or .47 Wh/$cm^3$, in accordance with our expectations for this size of cell.

The discharge at -40°C revealed the effect of the two layers of separator used in making the cells.

It is obvious from the data shown in Table 6 that the cells delivered at -40°C as much as 50% of the room temperature capacity with 1 mA/$cm^2$ discharge at 2.0 V cutoff line, while the discharge at 3 mA/$cm^2$ had to be extended to 1 V in order to realize that capacity. A large internal impedance of the cell is therefore solely responsible for the low discharge voltage at this low temperature. The reduction of the separator to one layer will reduce the cell internal impedance.

A further reduction of the internal impedance is possible by pre-evacuating the cells before dispensing the electrolyte, so that air bubbles between the electrodes are removed. A tighter packaging would further improve the discharge voltage of the cell, since the electrolyte resistance between the layers and the thickness of separators are the two major contributors to the overall impedance of fresh cells.

These cells were made with the conventional 0.34-inch thick flat cathodes. By using the GTE special procedure for thin electrodes, the total surface area of the electrodes could be doubled, thus further improving the rate capability of the cell at low temperatures. The lack of thin lithium foil, corresponding in capacity to the thin cathode, prevented us from running the first series of tests using higher surface area electrodes. Now that the source of the extra thin lithium has been secured, the next series of low temperature tests will be carried out with the same size cells having nearly a double surface area of electrodes and, expectedly, higher discharge voltage at -40°C and the same total current applied previously.

## SECTION IV

## ABUSE

Abuse testing has been performed on both cylindrical and prismatic cells. Included within this Interim Technical Report are the summary and results of both sets of tests. A report is being prepared for each set of tests which sets forth the procedure used, instrumentation setup, and data obtained. These two reports will be submitted as additional information by separate submittal.

### 1. CYLINDRICAL CELLS

Thirteen different environmental and abuse tests were conducted on cylindrical cells. They were:

1) Discharge to 3.0V cutoff
2) Salt Immersion
3) Discharge at Excessive Rates
4) Abusive Charging
5) Puncture
6) Crush
7) Overheating
8) Drop
9) Vibration (Bounce)
10) Shock
11) Incineration
12) Thermal Shock
13) Deactivation and Disposal

#### a. Discharge to 3.0V Cutoff

Twenty-four cells were discharged at the rate of $1mA/cm^2$ to the 3.0V cutoff line. Connectivity for discharge is shown in Figure 9. The group included the following types of cells:

1) 12 each of the standard size D cells, lithium-limited
2) 5 each of the double D size cells, lithium-limited
3) 7 each of the standard size D cells, carbon-limited

The average capacity obtained from D cells, lithium-limited, was 4.75 Ah with the high and low values being 5.67 Ah and 4.42 Ah, respectively. The theoretical capacity of these cells, based on the amount of lithium

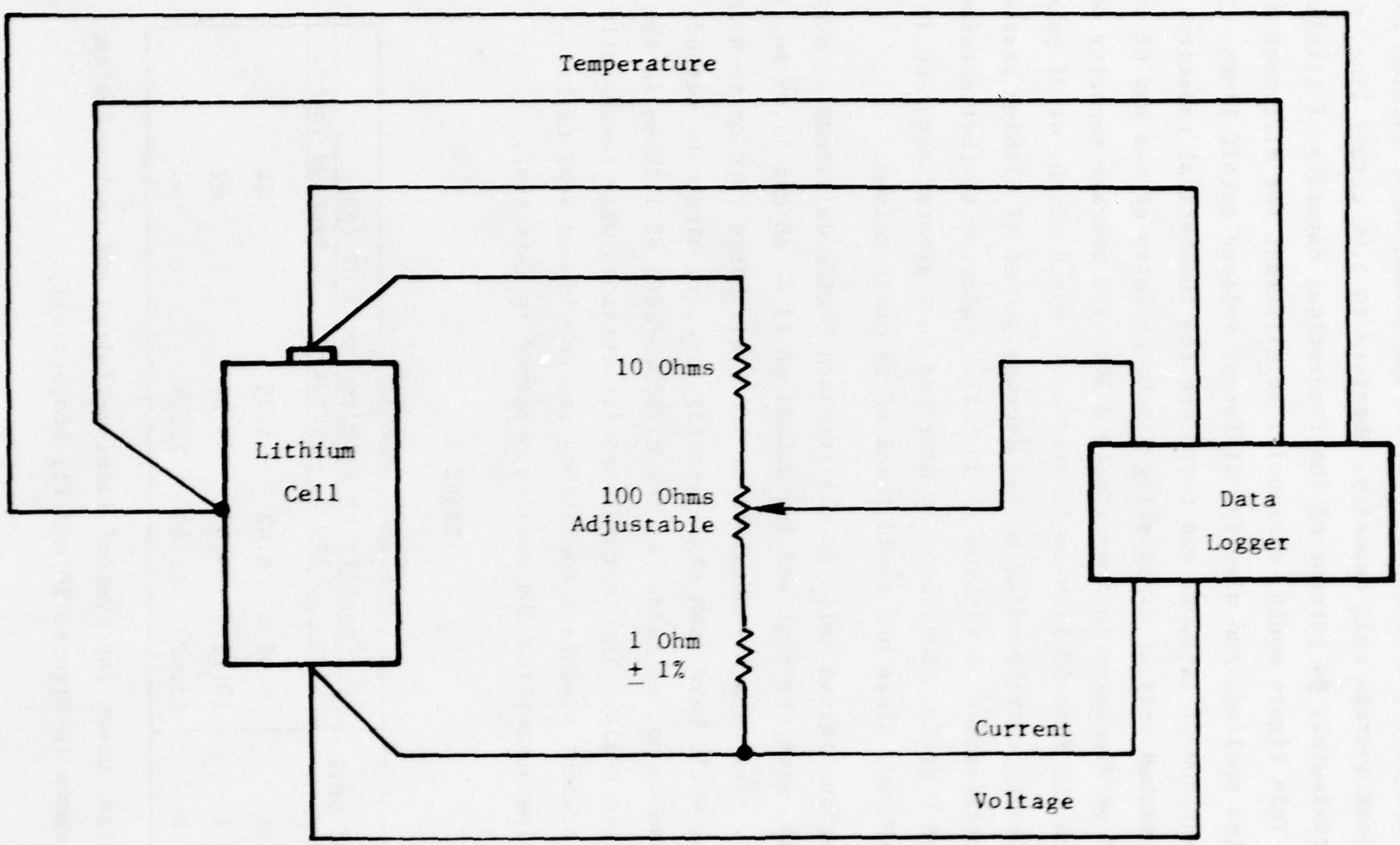


Figure 9. Discharge to Cutoff Connectivity

used, was 4.42 Ah with the possible variation of ± 5 percent from one cell to another, due to nonuniformity in the thickness of lithium foil. The resultant average cell capacity, obtained to 3.0V cutoff line, represents approximately 84 percent of the theoretical capacity of lithium present. This figure would, obviously, be different for different discharge rates applied, and also for different voltage cutoff lines. The total exhaustion of lithium, and therefore the theoretical capacity, could be reached only at diminishing discharge rates at the end of discharge and on discharge to approximate 0.5V. The average capacity obtained with the five DD lithium-limited cells was 9.66 Ah, or 92 percent of the capacity corresponding to the average amount of lithium present. A better utilization of lithium in DD cells, relative to that obtained in standard D cells, could only be ascribed to a greater accuracy in cutting lithium, since one could think of no other reason.

The carbon-limited cells in the standard D-size delivered an average of 12.74 Ah, with the high and low values of 13.42 Ah and 11.49 Ah, respectively. The capacity obtained at lower discharge rate or to a lower cutoff line would have been significantly greater, since the cathode polarization is not so sudden as the disappearance of lithium in the anode-limited cells. The average capacity obtained with these cells under the present discharge conditions are considered very high. Table 7 below summarizes the results obtained in this test.

TABLE 7

DISCHARGE CAPACITY

| Type of Cell | Capacity at 1 $mA/cm^2$ to 3.0V (Ah) | | | |
|---|---|---|---|---|
| | High | Low | Average | % Average Theor. |
| D,LL | 5.67 | 4.42 | 4.75 | 84 |
| DD,LL | 10.12 | 9.45 | 9.66 | 92 |
| D, CL | 13.42 | 11.49 | 12.74 | -- |

Discharge curves for typical lithium-limited and carbon-limited cells are shown in Figures 10 and 11, respectively.

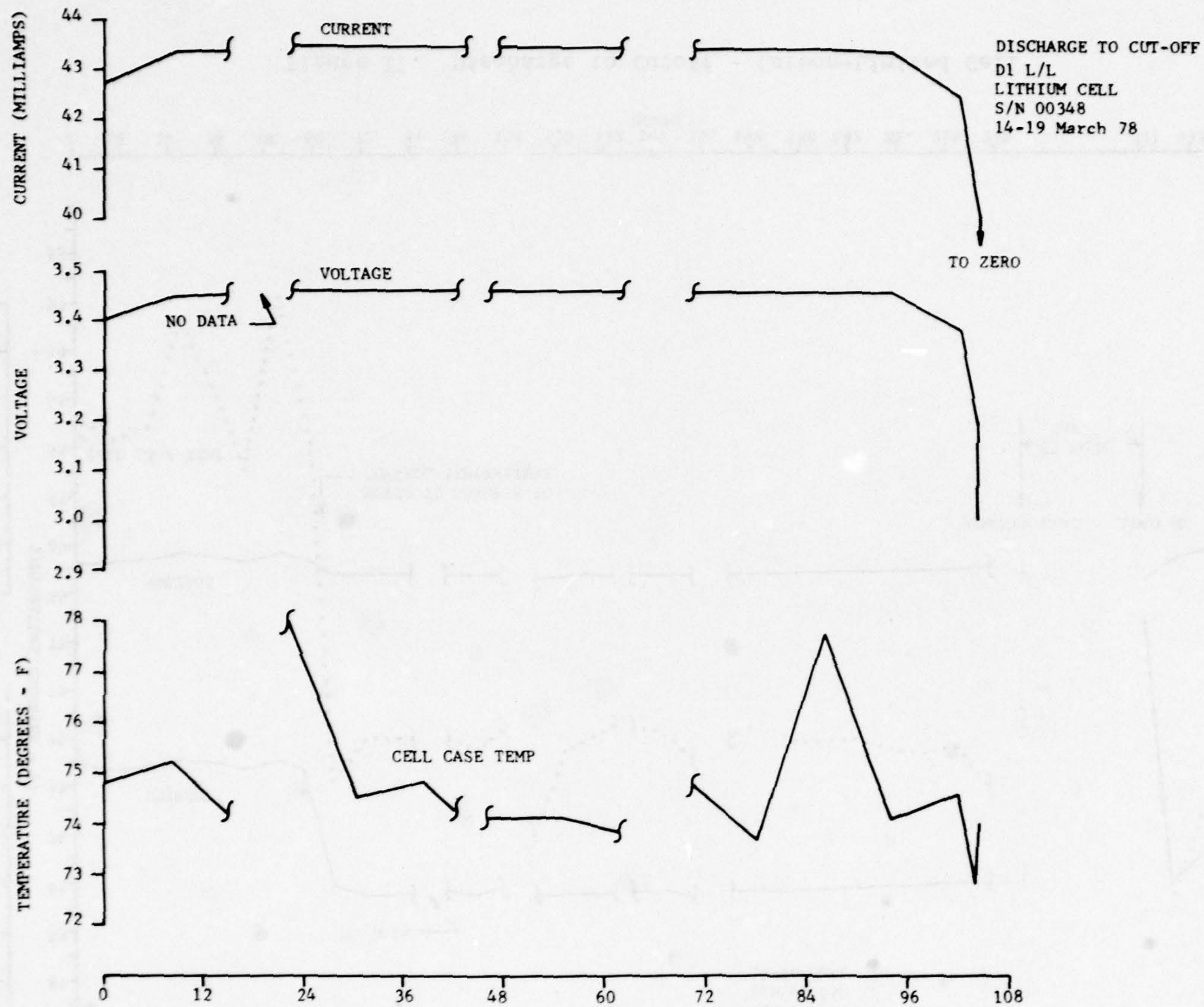


Figure 10. Discharge to Cutoff - Lithium-Limited Cell

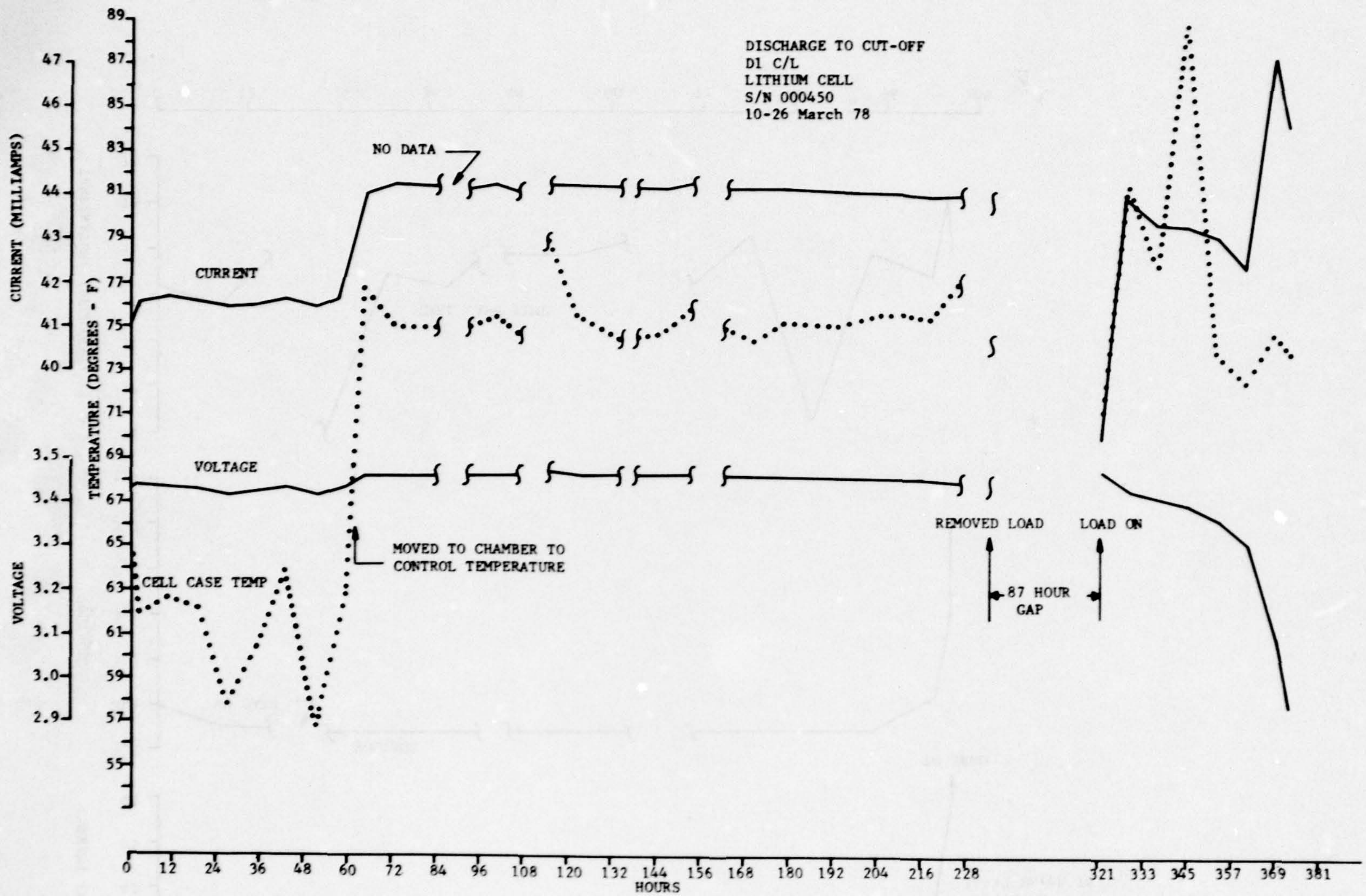


Figure 11. Discharge to Cutoff - Carbon-Limited Cell

b. Salt Immersion

One standard size D cell, lithium-limited, was subjected to the salt immersion test for 24 hours in 3% sodium chloride solution. No leakage was observed from the cell during the test period. The change in the ph of the salt solution from 4 to 6 during the test cannot be ascribed to leakage (the change in case of leakage would have been in the opposite direction). The corrosion of the + terminal must have been the result of an anode dissolution of the terminal material, caused by the electrolysis of the test solution by voltage of the cell itself. A further proof of the electrolytic process taking place outside the cell is the cell voltage drop to 3.44V measured immediately after the test. The cell recovered to the full OCV of 3.66V after cleaning, washing, and standing in the air to dry.

c. Discharge at Excessive Rates

Eight standard size D cells were subjected to an excessive discharge rate by shorting them through a 100 A, 50 mV shunt. Following is a list of types of cells used, in fresh and discharged states, one each at 25°C and 55°C:

1) 2 cells D, LL, fresh
2) 2 cells D, CL, fresh
3) 2 cells D, LL, discharged
4) 2 cells D, CL, discharged.

No venting, rupture, or explosion was observed during the tests with any of the eight cells. The maximum temperature of 106°C was achieved, 7 to 8 minutes from the beginning of discharge at the skin of the fresh cell, which was thermally equilibrated at 55°C in a closed test chamber prior to discharge. The maximum discharge current was 7 A after one minute of discharge for fresh cells. The values were lower for all cells that were tested in discharged states or at the temperature of the test chamber of 25°C. A slow decrease in the discharge current, accompanied by the drop in temperature, was observed after these maxima were passed.

d. <u>Abusive Charging</u>

Charging tests were performed on standard size D cells of the following types:

1) constant current charging: 2 ea., D, LL, fresh
   2 ea., D, LL, discharged
2) constant voltage charging: 2 ea., D, LL, fresh
   2 ea., D, LL, discharged.

Two different charging regimes were applied to both fresh and previously discharged cells, one at constant voltage of 4.1 V and the other at a constant current of 44 mA. The discharge current and the cell's case temperature were monitored during the constant current charging. The tests were carried out for several hours in each of the tests, i.e., until the cells reached stable conditions.

The charging of fresh cells under either of the two charging conditions (Figures 12 and 13) showed a slow increase in temperature of $0.5^{o}C/$ hour. The two charging regimes did not differ significantly, as far as the electric characteristics of cells are concerned. Under the constant voltage of 4.1 V, the high charging current over 100 mA decayed rapidly and stabilized below 20 mA, while under a constant current of 44 mA the charging voltage remained between 4.0 and 4.1 V over a period of eight hours. A slight difference in the steady state charging conditions, following the initial period, can be attributed to individual differences in the geometry of the cells, as related to the cell's ability to recombine the products of charging formed on the two electrodes. Of the two cells tested under each of the charging conditions only one was represented in each of the diagrams, since there were no substantial differences in the behavior of the same type of cells tested under the same charging conditions. Charging of the discharged cells under each of the two charging conditions is shown in Figures 14 and 15, respectively. The constant voltage charging of discharged cells showed much higher charging current than those observed in charging of the fresh cells, with a slight initial difference in the behavior of the two cells tested (Figure 11). As a result, the rate of temperature increase was much greater, amounting to $2^{o}C$ per hour over a period of five hours. A slow leveling off in the temperature increase with time is probably influenced by both of the two factors: the cooling rate and the reduction of the charging current.

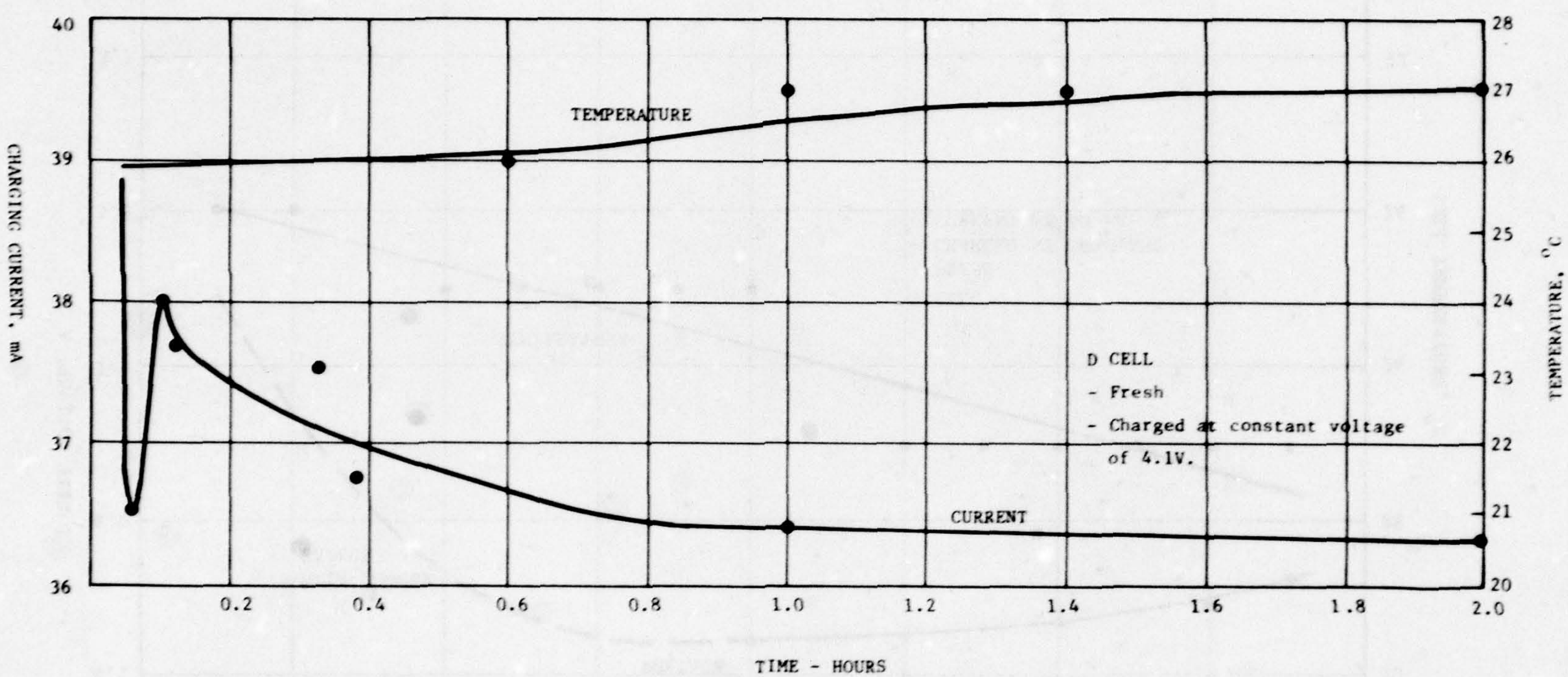


Figure 12. Constant Voltage Charging of Fresh Cell

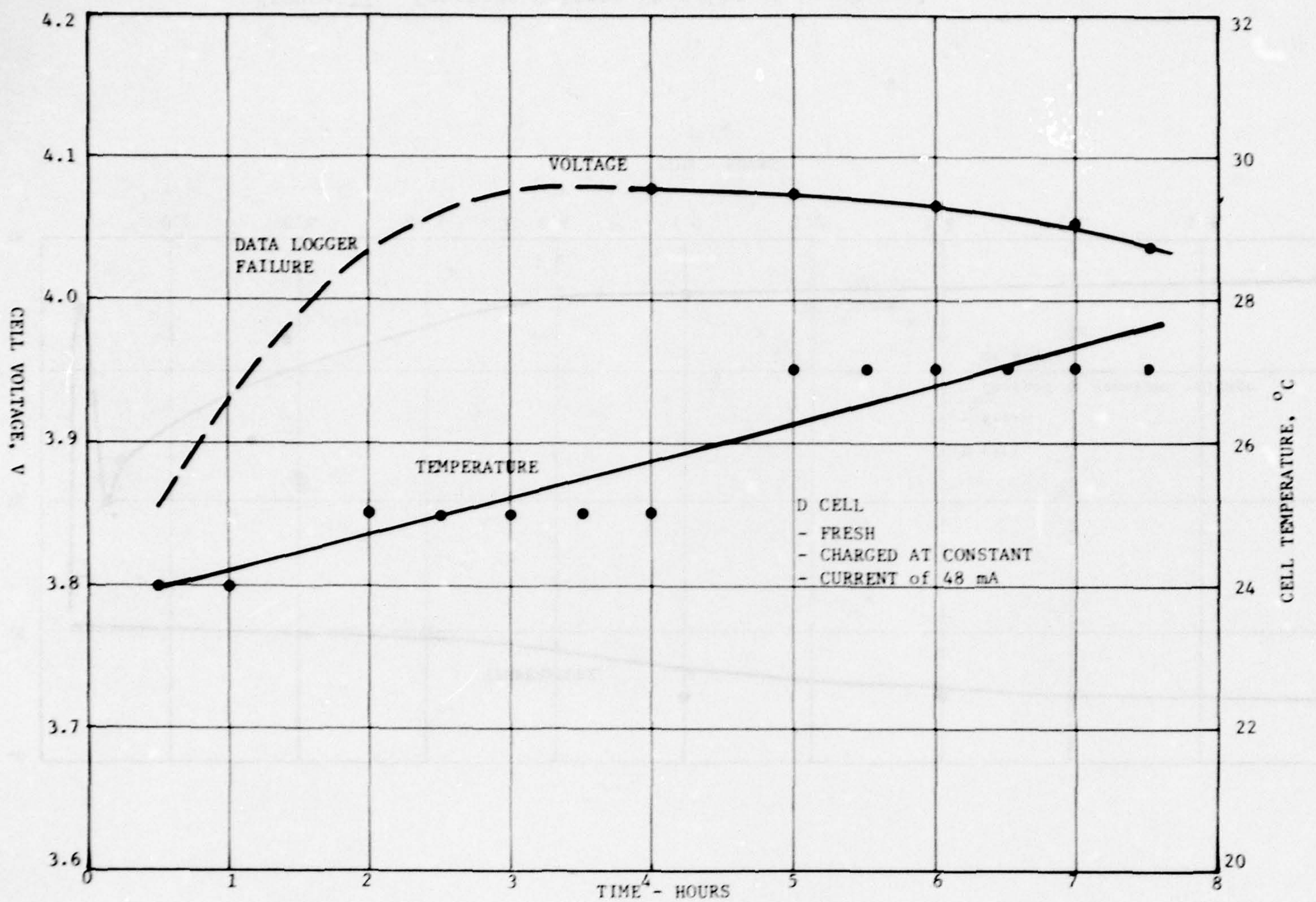


Figure 13. Constant Current Charging of Fresh Cell

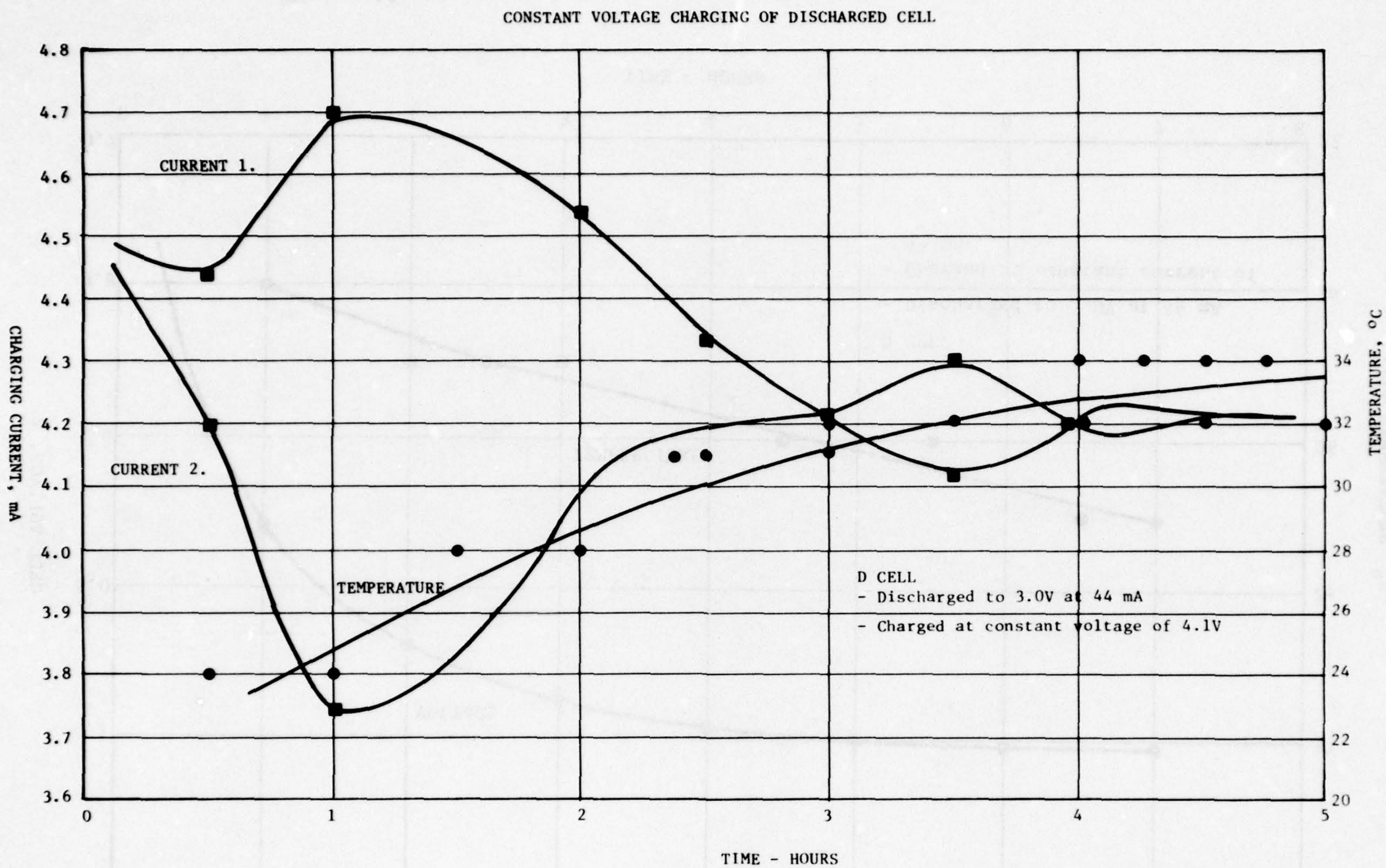


Figure 14. Constant Voltage Charging of Discharged Cell

CONSTANT CURRENT CHARGING OF DISCHARGED CELL

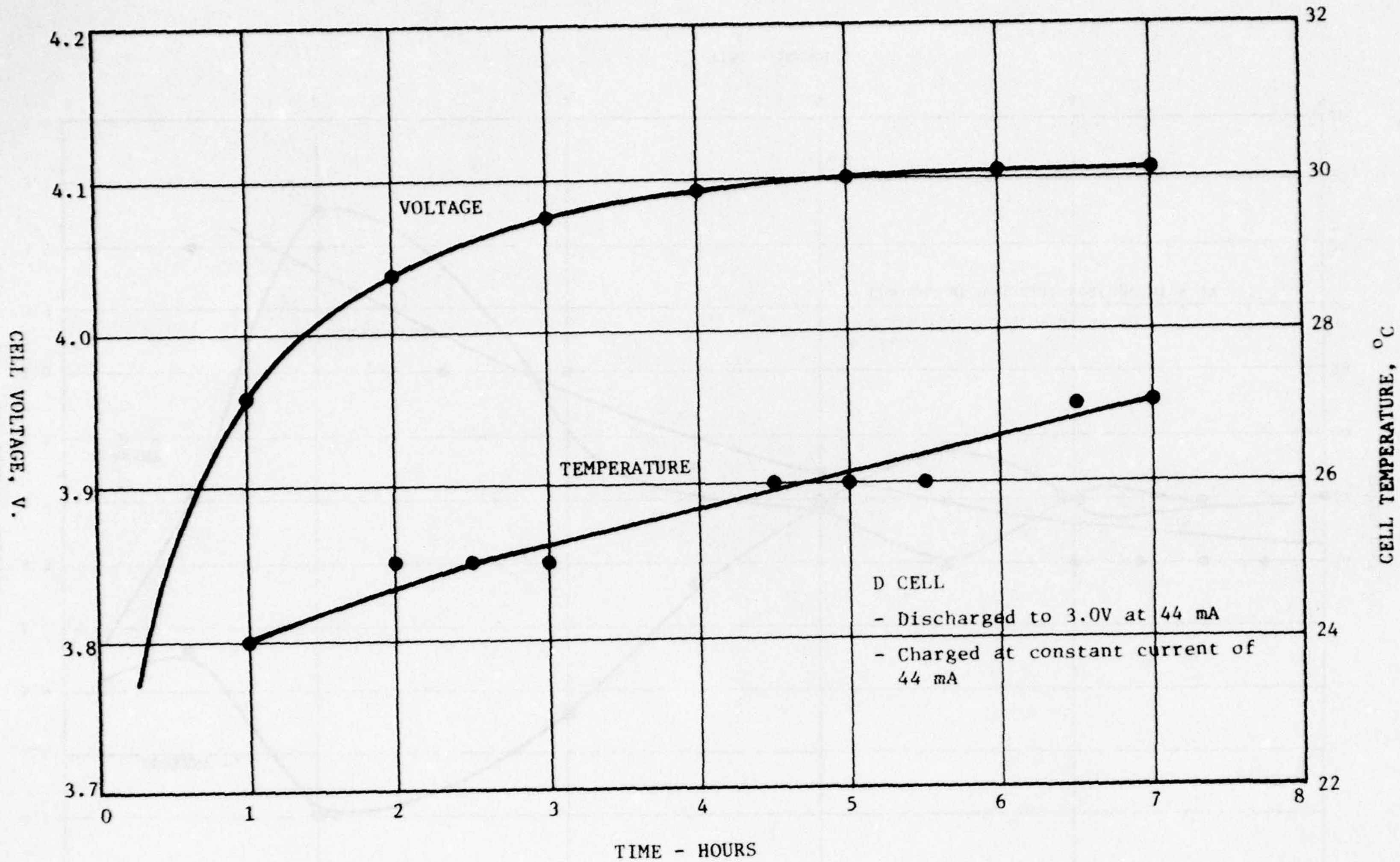


Figure 15. Constant Current Charging of Discharged Cell

The constant current charging of discharged cells closely resembled the charging of fresh cells under the same conditions. A steady increase in the cell's case temperature of 0.5°C/hour was also observed with these cells.

No rupture, leakage, bulging, or explosion was experienced with any of the cells used in the course of the abusive charging test.

The experience gained in these tests agrees with the observations made during the charging tests with the 2000 Ah rectangular cells, as well as with the reported observations made by other companies (Honeywell, Mallory, Power Sources Conference, Atlantic City, N. J., June 1978). The tentative explanation is that the chlorine generated on the cathode and fresh lithium generated on the anode during charging combine quickly forming LiCl, so that the cumulative effect of charging is just the formation of heat within the cell, corresponding to the heat of reaction of chlorine and lithium, with some contribution of ohmic heating due to the internal impedance of the cell.

e. Puncture

Five cells of the following type and discharge status were subjected to a puncturing test:

1) 1 each, fresh, D, CL room temperature
   D, LL room temperature

2) 1 each, discharged D, CL
   D, LL
   DD, LL

The cells were punctured with an electric drill perpendicular to the side, 1/4-inch deep or until short circuited. No venting, rupture, or explosion was observed. The maximum cell case temperature was 75°C for a fresh DD cell punctured at the ambient temperature of 15°C, 20 minutes after the puncture. Lithium-limited cells discharged at 1 $mA/cm^2$ to 3.0 V cutoff showed only one to two degrees C increase in temperature, four to five minutes after puncture. The carbon-limited cells, discharged under the same conditions, showed an increase in temperature of ten to twelve degrees C, 10 to 15 minutes after puncture. Figures 16 and 17 show the discharge characteristics of discharged and fresh lithium-limited cells.

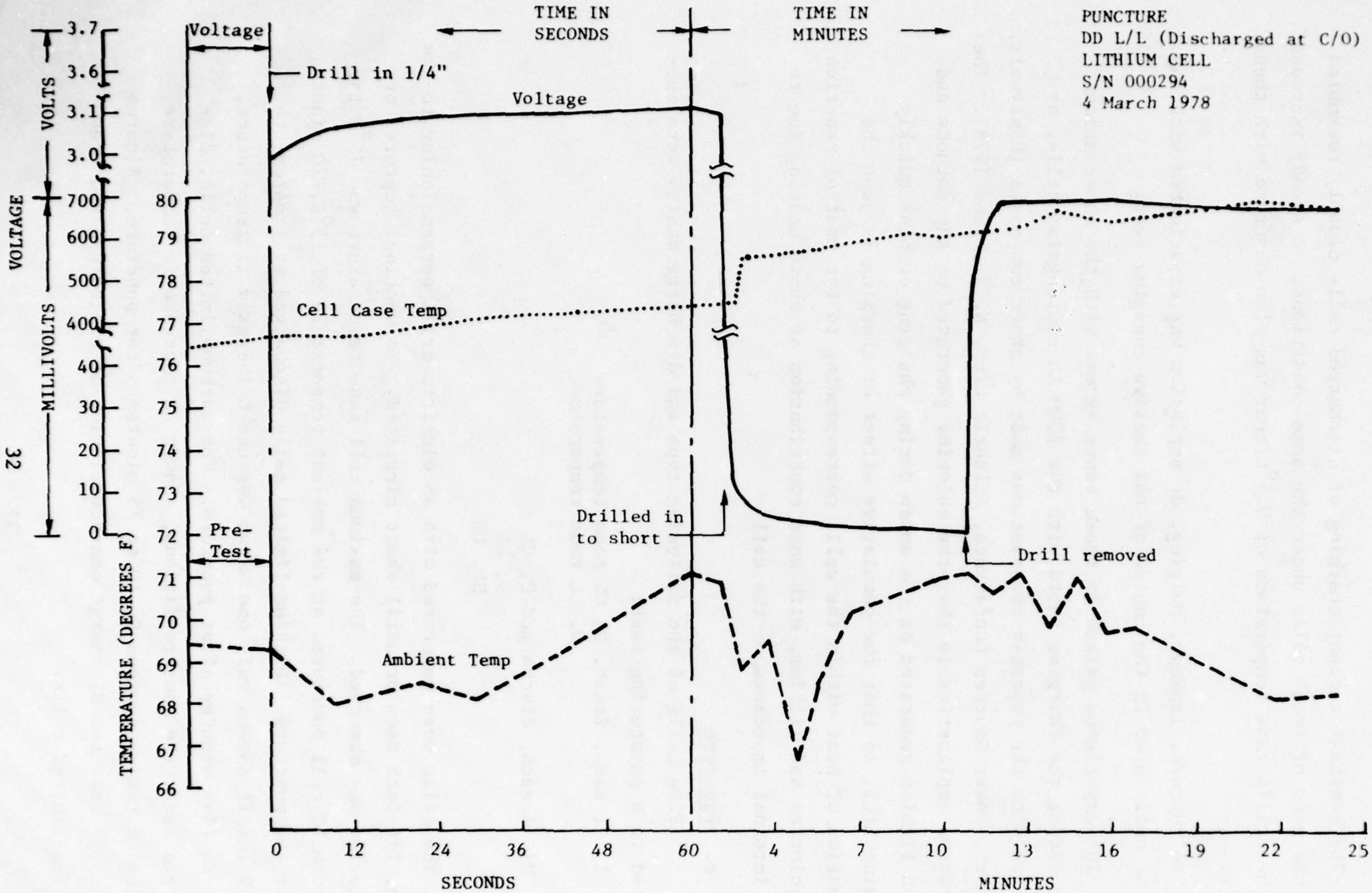


Figure 16. Discharge Characteristics - Discharged Lithium Cell

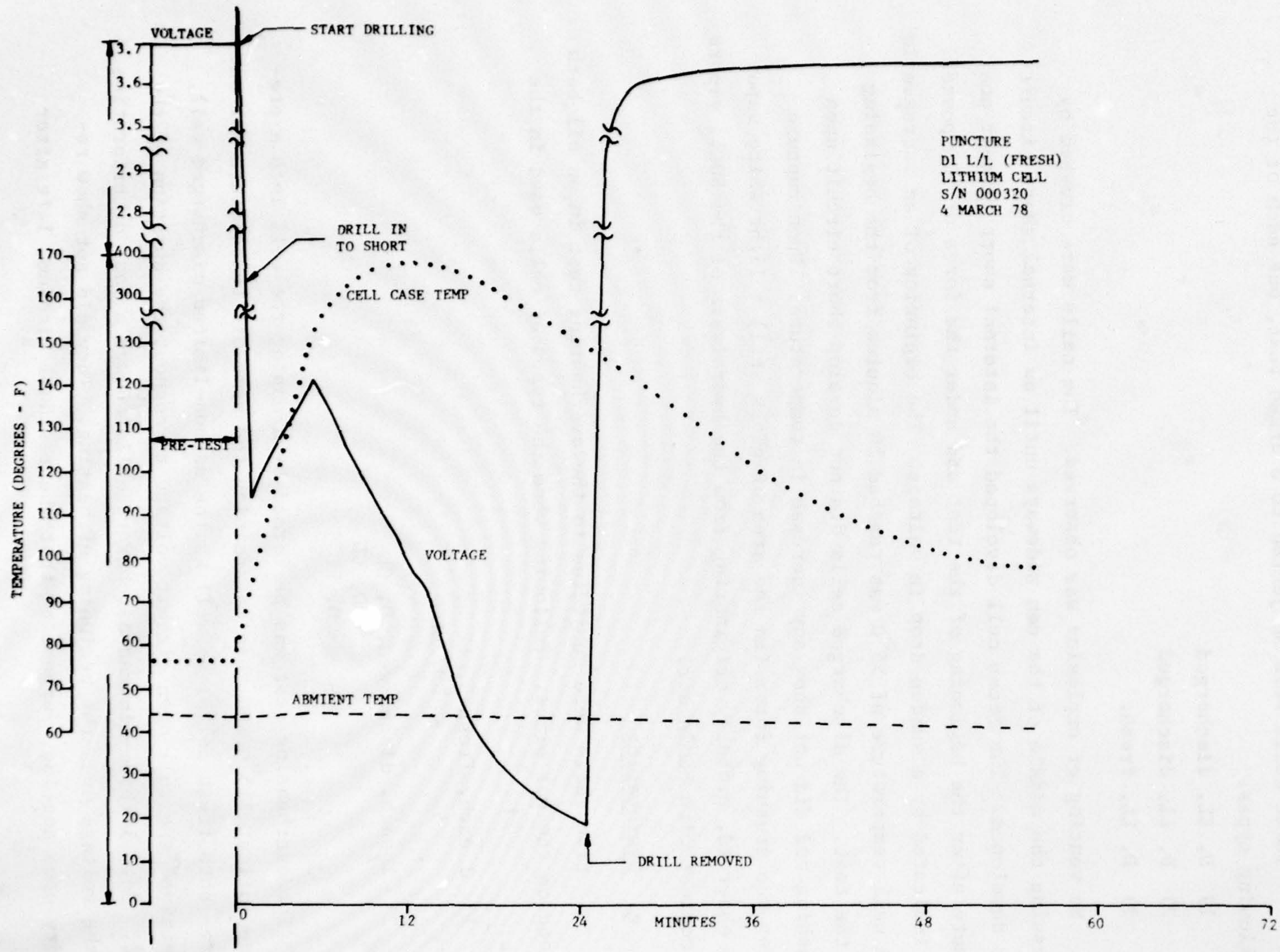


Figure 17. Discharge Characteristics - Fresh Lithium Cell

f. Crush

Three cells were subjected to a crush test, one each of the following types:

1) D, CL, discharged
2) D, LL, discharged
3) D, LL, fresh.

No venting or explosion was observed. The cells were crushed by pressing the middle of the can sideways until an internal short circuit was developed. The fresh cell developed the internal short circuit one minute after the beginning of the test and under the force of 900 pounds, as indicated by a sudden drop in voltage. The beginning of an increase in the cell temperature of $55^{\circ}C$ was reached 16 minutes from the beginning of the test. The discharged cells did not develop short circuit upon crushing and did not show any increase in temperature. Upon rupture under the crushing force (in the area of glass seal) a light white vapor was observed, probably originating from the hydrolysis of the $SOCl_2$ vapors in contact with humid air.

g. Overheating

Five cells were subjected to the overheating test in an oil bath placed on the hot plate. Following were the types of cells used in the test:

1) 1 each, fresh D, LL
DD, LL

2) 1 each, discharged, D, CL
DD, LL
D, LL

The overheating test was performed by dropping the cell into a preheated oil at $115^{\circ}C$ and then maintaining the same oil temperature for one hour. Both fresh cells, as well as the carbon-limited discharged cell, maintained the full open circuit voltage throughout the duration of the test. Both lithium-limited discharged cells showed a fast deterioration of the voltage upon the beginning of heating. They did not show recovery upon cooling, suggesting that the residual lithium, left after discharge, was consumed in a direct chemical reaction during the overheating test, resulting in a permanent loss of the cell's open circuit voltage. None of the cells vented, ruptured, or exploded.

h. Drop

Two cells of the standard size D, LL, one fresh and one discharged, were subjected to a 6-foot drop. The open circuit voltage was measured before the drop test and then monitored for 40 minutes after the drop. Cell skin temperature was also monitored following the drop.

No venting, bursting, or explosion occurred as a result of the drop. Also, no change in either the open circuit voltage or cell skin temperature was observed.

i. Vibration (Bounce)

The vibration test was conducted in accordance with MIL-STD-810C, Method 514.2, Procedure X1, Part 2, using four cells, one each of the following types:

1) 1 cell, DD, LL, fresh
2) 1 cell, D, LL, fresh
3) 1 cell, DD, LL, discharged
4) 1 cell, D, LL, discharged.

The cells were tested on the machine designed to meet the requirements of the above mentioned MIL specification. The test duration was 90 minutes in horizontal position, followed by 90 minutes in vertical position for each of the four cells. The cells' skin temperatures and open circuit voltages were monitored througnout the duration of the test. No change of voltage or temperature was observed during the tests. The specimens did not leak, vent, rupture, or explode.

j. Shock

The shock tests were conducted using four cells of the following types:

1) 1 cell, DD, LL, discharged
2) 1 cell, D, LL, discharged
3) 1 cell, DD, LL, fresh
4) 1 cell, D, LL, fresh.

The shock pulses were terminal sawtooth in shape, 100 mg in magnitude and 6 milliseconds in duration. The shock machine was a drop-impact type with a table weight of approximately 1500 pounds. The impact material was cone-shaped lead pellets designed to produce a particular shock pulse. A typical discharge curve for a lithium-limited cell is shown in Figure 18.

Each cell's open circuit voltage and skin temperature were monitored during the test. No change in temperature or voltage was observed. The cells did not leak, rupture, vent, or explode.

k. Incineration

The incineration test was conducted using three cells, one each of the following type:

1) 1 cell, D, LL, fresh
2) 1 cell, D, LL, discharged
3) 1 cell, D, CL, discharged.

The cells were incinerated in the flames of burning diesel oil, the temperature of which was well in excess of the melting point of lithium. The fresh cell exploded during this test as expected. Both of the discharged cells vented through the positive terminal as expected.

The test results suggest that a fast spontaneous reaction was initiated between the cell active components as a result of heating to a high temperature, leading to an explosion. The discharged cells, with a minimal amount of active components left after discharge, expanded slowly during the heating until the cell's top was sufficiently distorted to crack the glass and open the cell to the atmosphere.

l. Thermal Shock

Thermal shock tests were conducted using three cells, one each of the following types:

1) 1 cell, D, LL, fresh
2) 1 cell, D, CL, discharged
3) 1 cell, D, LL, discharged.

The thermal shock test was conducted in accordance with MIL-STD-810C, Method 503.1. The cells were equilibrated for four hours inside a chamber at 63$^{o}$C and then within a maximum of five minutes, transferred to another chamber and equilibrated at -54$^{o}$C, where they were left for another four

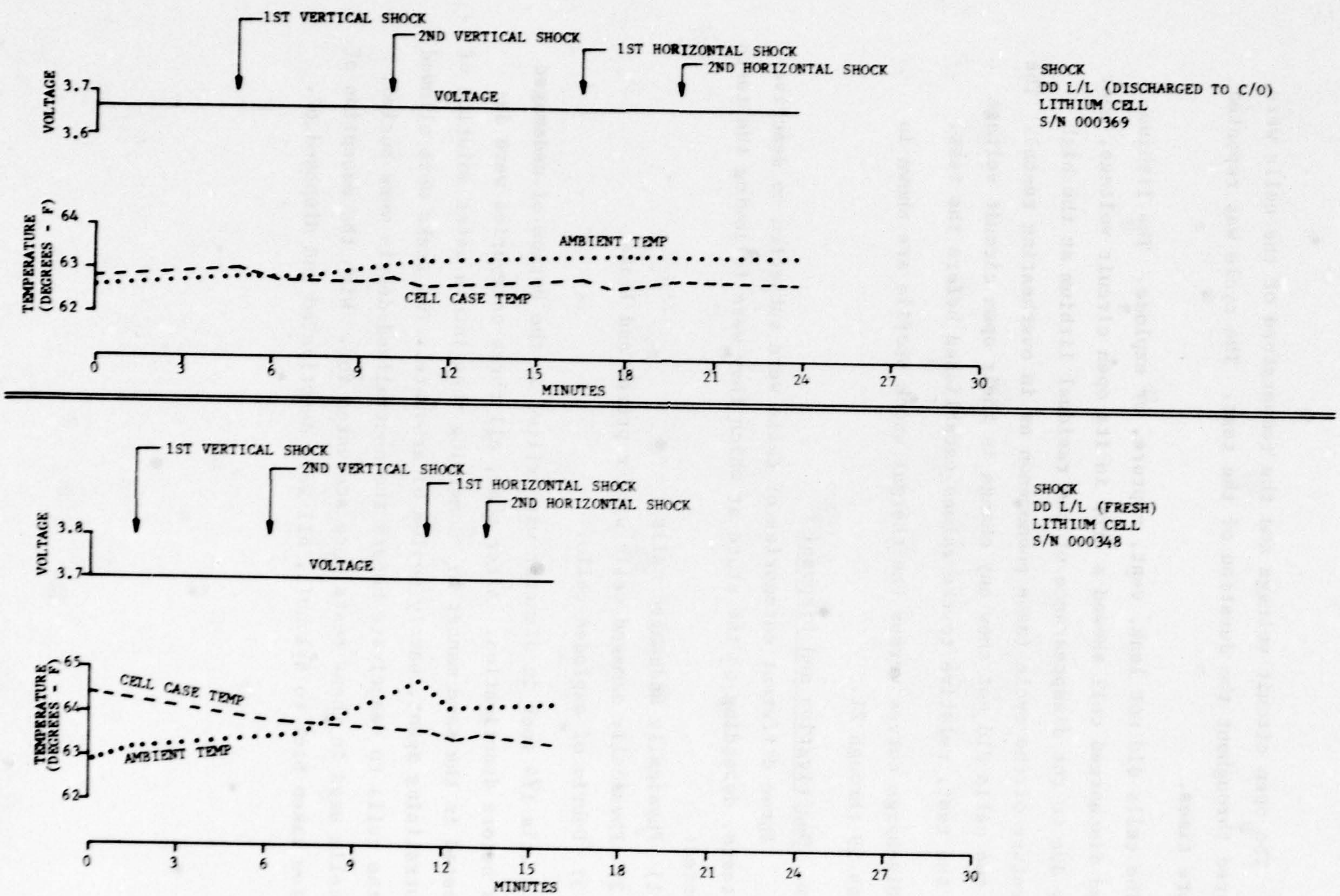


Figure 18. Discharge Curves for Lithium Cell - Shock Test

hours. The open circuit voltage and the temperature of the cells were monitored throughout the duration of the test. The cycle was repeated two more times.

The cells did not leak, vent, rupture, or explode. The lithium-limited discharged cell showed a drop in its open circuit voltage, most likely due to the disappearance of the residual lithium at the high temperature of the cycle (same phenomenon as in overheating tests). The other two cells did not show any change in their open circuit voltage after the test, relative to the values established before the test.

Discharge curves versus the thermal shock profile are shown in Figures 19 through 21.

m. Deactivation and Disposal

Three different categories of cells were subjected to deactivation tests, depending on the state at which they were following the tests conducted:

1) Physically undamaged cells
2) Physically damaged cells with ruptures and leaks
3) Debris of exploded cells.

A hole 1/4 inch in diameter was drilled in the bottom of undamaged cells before deactivation. After that, all three categories were deactivated in the same manner by submerging them into a water solution of a neutralizing agent, namely sodium bicarbonate. Two weeks were allowed for the cells to deactivate before the neutralized debris were buried. All cells used in these tests were accounted for. With the exception of the few taken back to Sylvania, all were deactivated and disposed of.

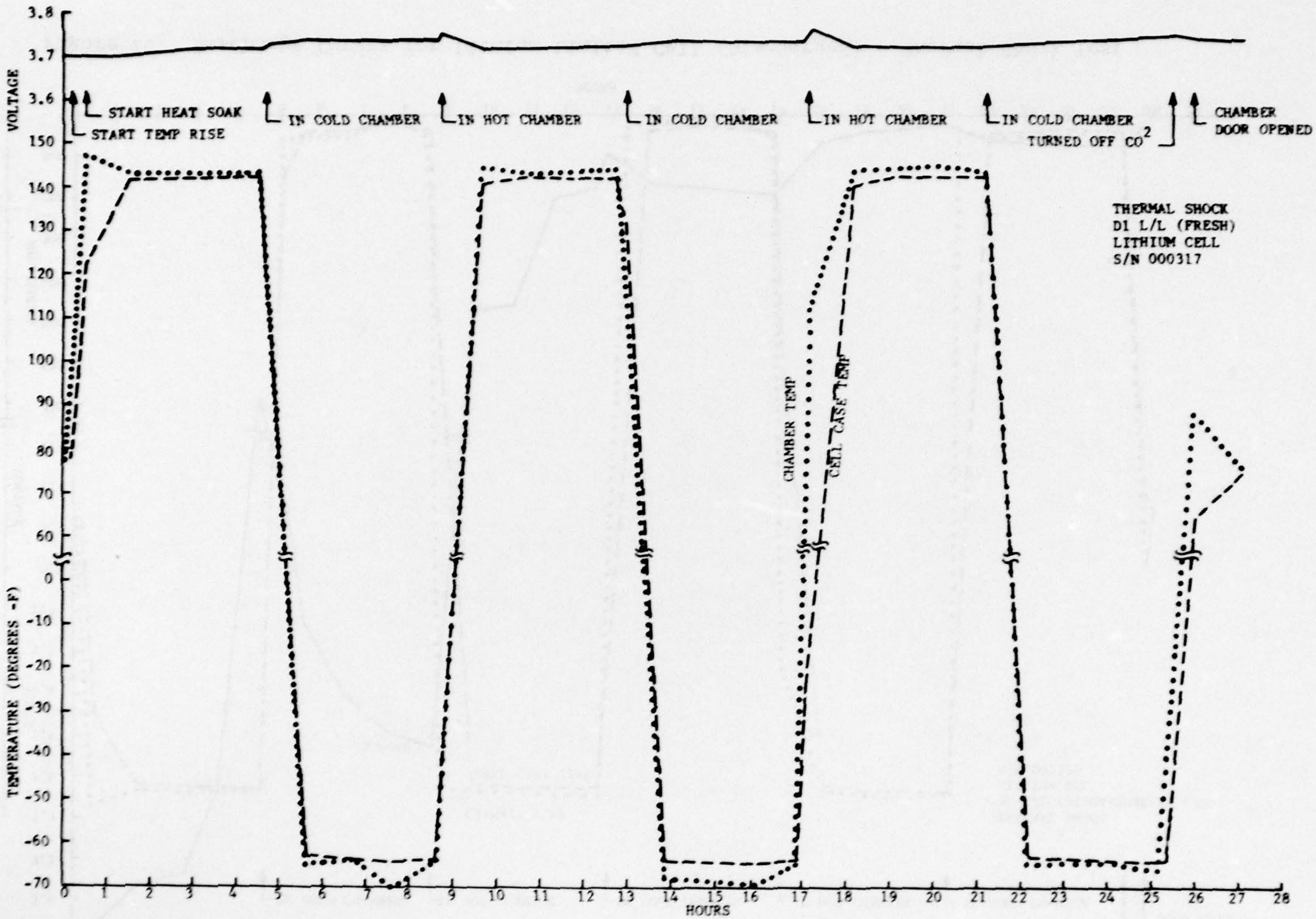


Figure 19. Discharge Curves for Lithium-Limited Cell (Fresh) - Thermal Shock Test

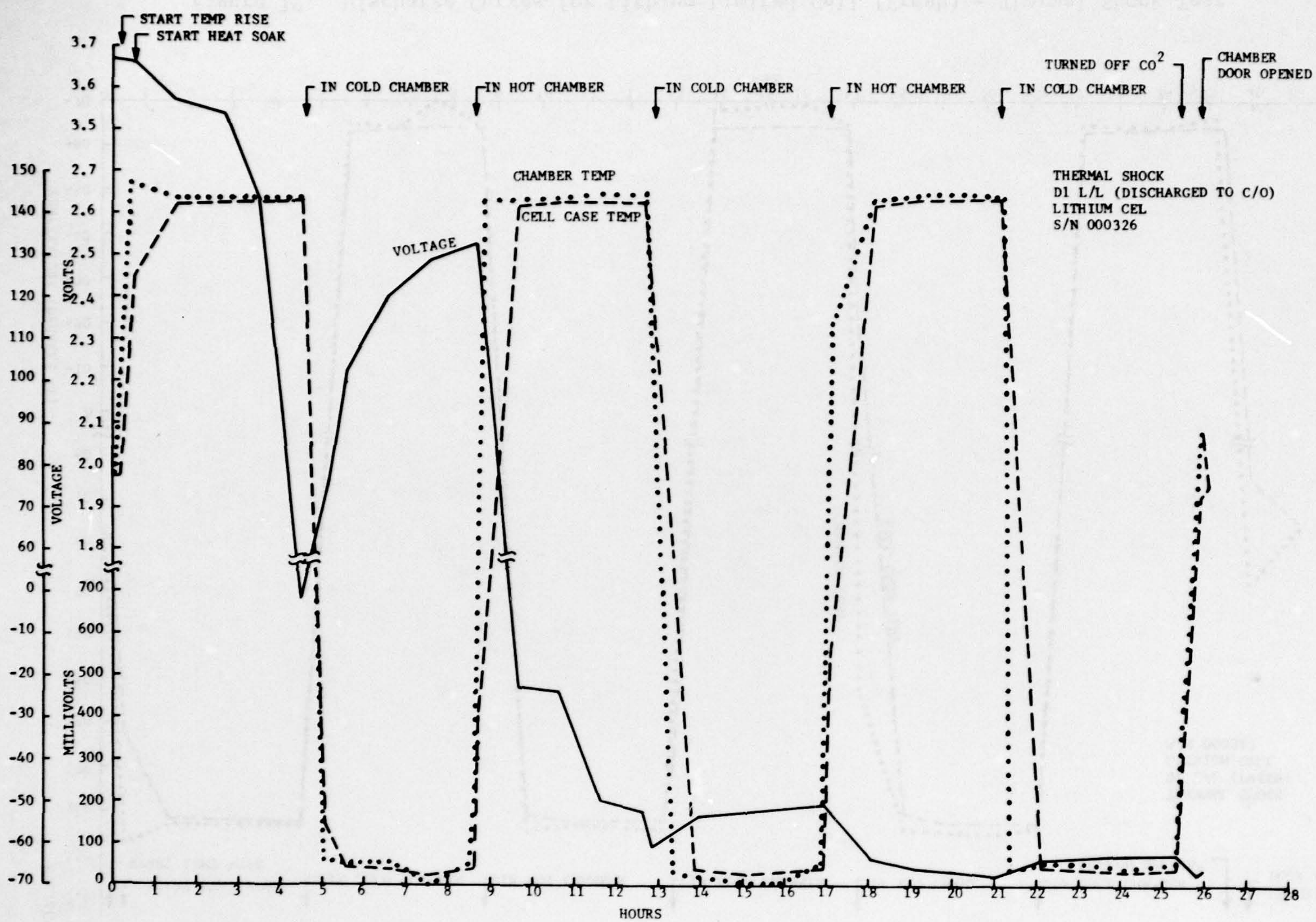


Figure 20. Discharge Curves for Lithium-Limited Cell (Discharged) - Thermal Shock Test

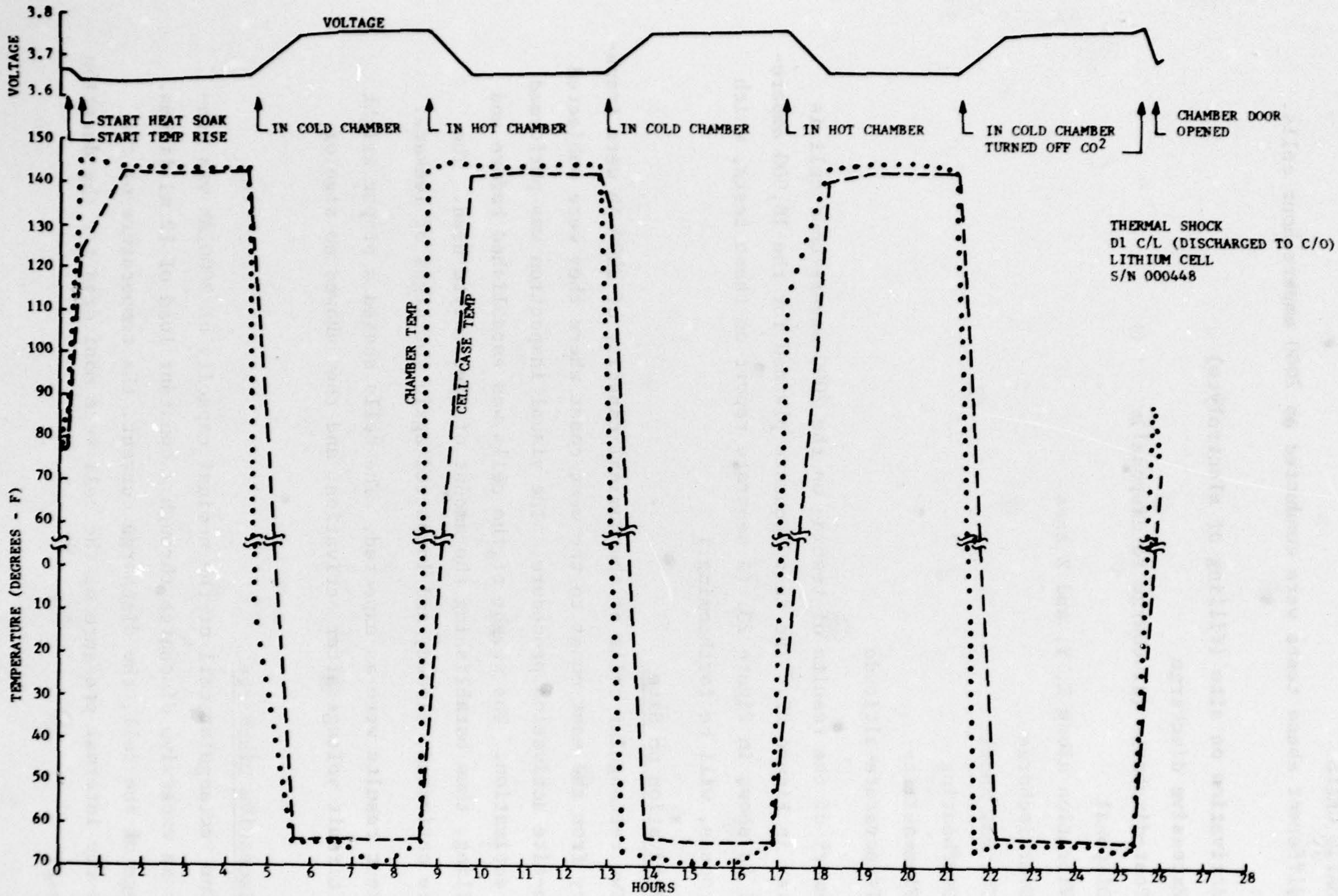


Figure 21. Discharge Curves for Carbon-Limited Cell (Discharged) - Thermal Shock Test

2. PRISMATIC CELLS

Ten different abuse tests were conducted on 2000 ampere-hour cells. They are:

1) Activation on site (filling of electrolyte)
2) Excessive discharge
3) Post-discharge (discharge to disposal)
4) Disposal
5) Vibration along X, Y, and Z axes
6) Overdischarge
7) Thermal Shock
8) Overheating
9) Flammability
10) Temperature-altitude

A summary of the results of testing on the 2000 ampere-hour cell is illustrated in Figure 22. The test sequence planned for the 10,000 ampere-hour cell is shown in Figure 23. (A separate report on these tests, which are in process, will be forthcoming.)

a. <u>Activation on Site</u>

Two rectangular cells of the nominal capacity of 2000 Ah were transported dry from the east coast to the west coast where they were subjected to the on-site activation procedure. The visual inspection was performed prior to activation. The weight of the cells was established before and after filling, thus establishing the amount of electrolyte used. The cells were activated, closed, and inspected again for signs of leakage.

The test results were as expected. The cells showed a proper weight and open circuit voltage after activation, and they showed no sign of leakage.

b. <u>Excessive Discharge</u>

One rectangular cell of the nominal capacity of 2000 Ah was subjected to an excessive discharge through a constant load of 12 milliohms. The voltage of the cell, the discharge current, the temperature of the case, and the internal pressure of the cell were monitored for the duration of the test.

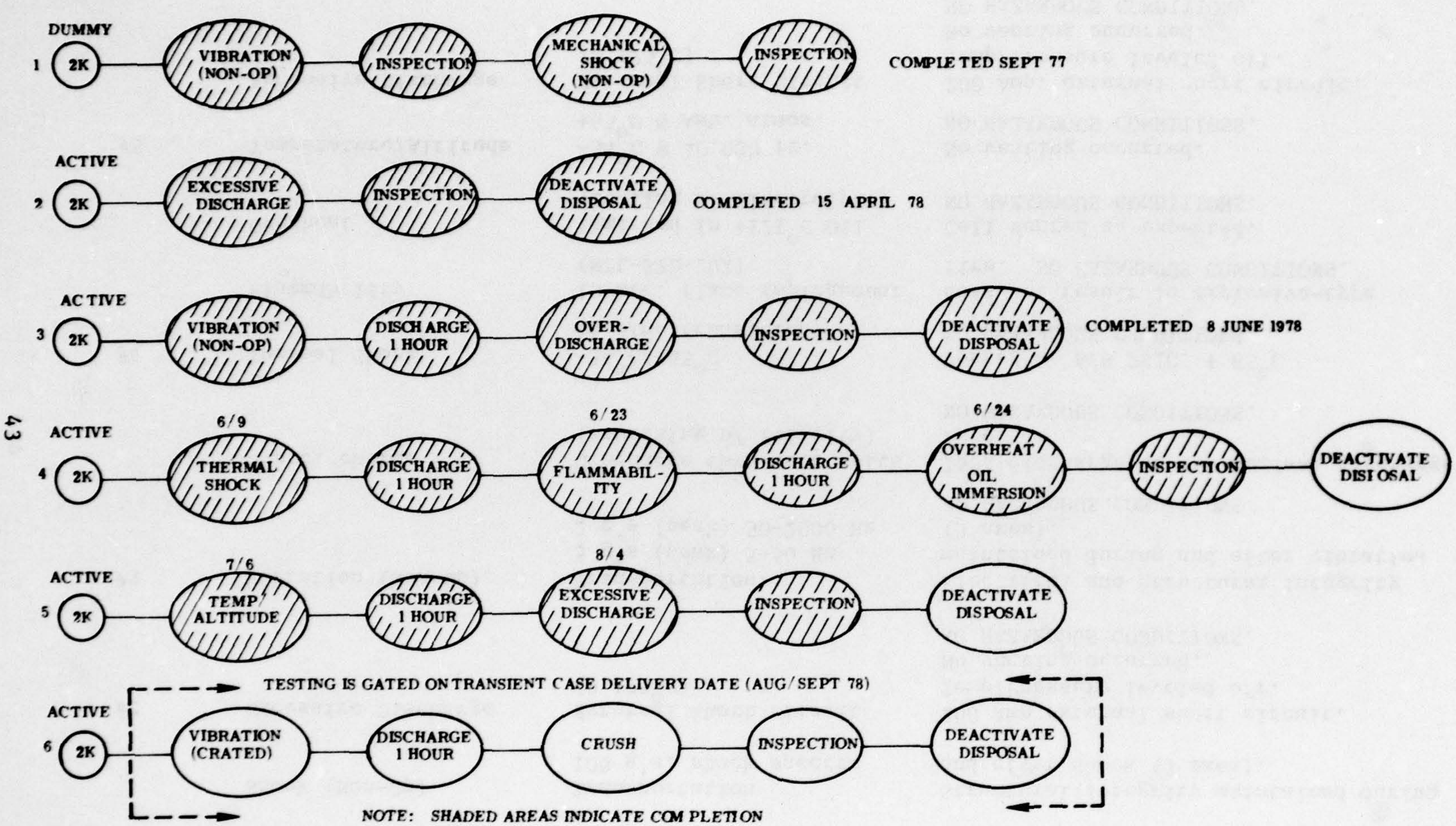


Figure 22. Test Flow and Description - 2,000 Ah Prismatic Cells

| SPECIMEN | TEST | CONDITION | RESULT |
| --- | --- | --- | --- |
| #1 (Dummy) | Vibration (Non-Op) | Transportation<br>5 g's (peak) 5-50 Hz<br>2 g's (peak) 50-2000 Hz | Structural integrity maintained during and after vibration (3 axes). |
| | Shock (Non-Op) | Transportation<br>100 g's, shock spectra | Structural integrity maintained during and after shock (3 axes). |
| #2 | Excessive Discharge | External Short Circuit<br>(@ +25°C) | 200 Amp external short circuit.<br>Temp/Pressure leveled off.<br>No venting occurred.<br>NO HAZARDOUS CONDITIONS. |
| #3 | Vibration (Non-Op) | Transportation<br>5 g's (peak) 5-50 Hz<br>2 g's (peak) 50-2000 Hz | Electrical and structural integrity maintained during and after vibration (3 axes).<br>NO HAZARDOUS CONDITIONS. |
| | Overdischarge | Discharge thru zero volts<br>(Reversing of Polarity) | 150% discharge at the nominal discharge rate.<br>NO HAZARDOUS CONDITIONS. |
| #4 | Thermal Shock | -54°C/+65°C<br>(5 min. transition) | Vented at 6.9 PSIG, + 65°C<br>NO HAZARDOUS CONDITIONS. |
| | Flammab lity | 15 sec. flame impingement<br>(MIL-STD-202) | Does not result in explosive-type fire. NO HAZARDOUS CONDITIONS. |
| | Overheat | Immersed in +121°C Oil<br>(Boiling of Electrolyte) | Cell vented as expected.<br>NO HAZARDOUS CONDITIONS. |
| #5 | Temperature/Altitude | -54°C @ 40,000 ft.<br>+65°C @ Amb. Atmos. | No venting occurred.<br>NO HAZARDOUS CONDITIONS. |
| | Excessive Discharge | External Short Circuit<br>(@ +25°C) | 200 Amp. external short circuit.<br>Temp/Pressure leveled off.<br>No venting occurred.<br>NO HAZARDOUS CONDITIONS. |

Figure 22. Test Flow and Description - 2,000 Ah Prismatic Cells (cont)

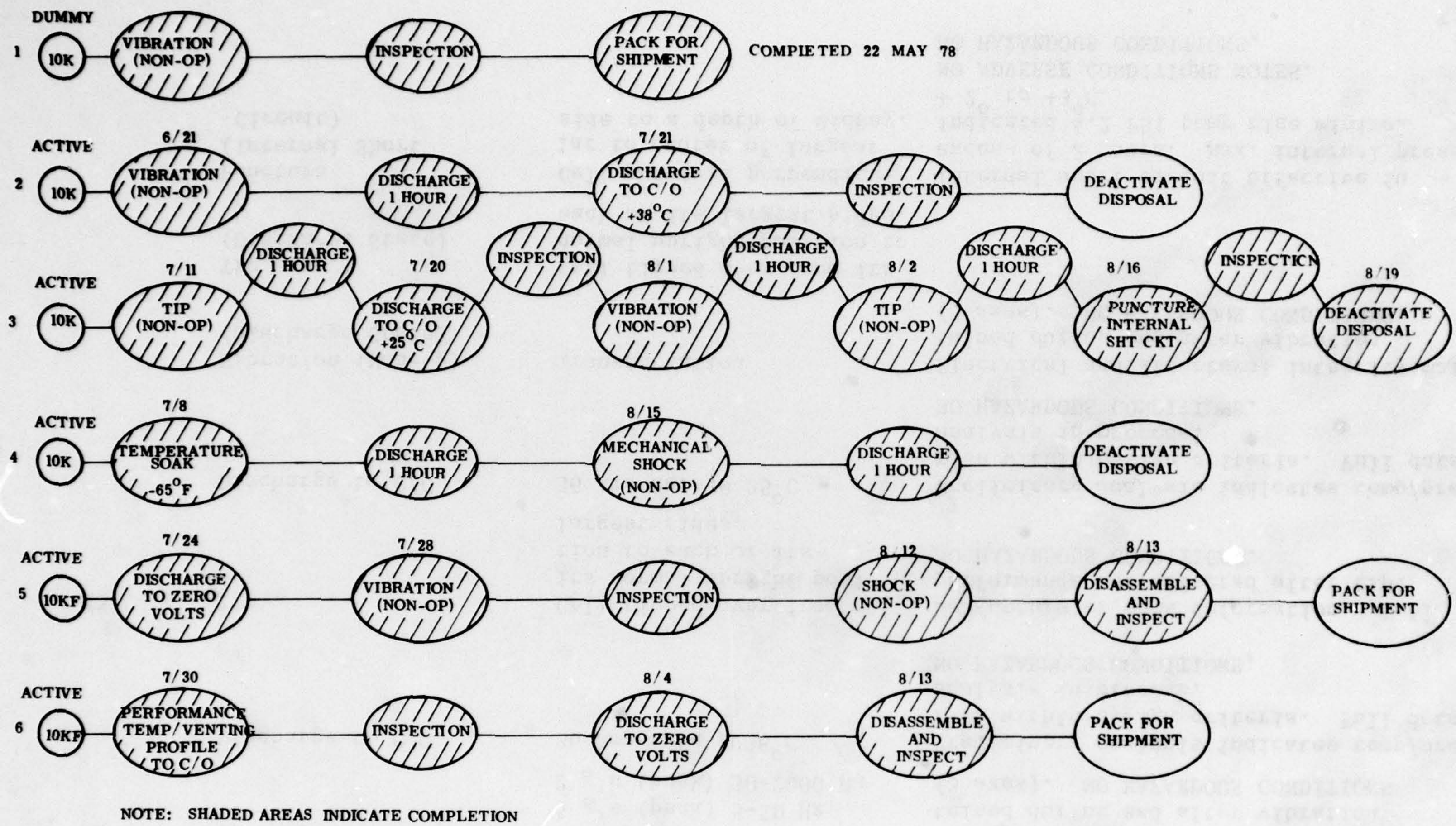


Figure 23. Test Flow and Description - 10,000 Ah Prismatic Cells

| SPECIMEN | TEST | CONDITION | RESULT |
|---|---|---|---|
| #1 | Vibration (Non-Op) Dummy | Transportation<br>5 g's (peak) 5-50 Hz<br>2 g's (Peak) 50-2000 Hz | Structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS. |
| #2 | Vibration (Non-Op) | Transportation<br>5 g's (peak) 5-50 Hz<br>2 g's (peak) 50-2000 Ha | Electrical and structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS |
| | Discharge to C/O | 36 Amp Rate @ 38°C | Preliminary analysis indicates temp/press. rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS. |
| #3 | Tip | Cell tipped over from its normal upright position to each of its largest sides. | No rupture or case deformation. Cell performance not affected after tip. NO HAZARDOUS CONDITIONS. |
| | Discharge to C/O | 36 Amp Rate @ 25°C | Preliminary analysis indicates temp/press. rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS. |
| | Vibration (Non-Op) (Discharge State) | Transportation | Electrical and structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS. |
| | Tip (Discharge State) | Cell tipped over from its normal upright position to each of its largest sides. | |
| | Puncture (Internal Short Circuit) | Cell puncture perpendicular to center of largest side to a depth of midway. | Internal short circuit effective in excess of 2 hours. Max. internal press. indicated 4.2 PSI temp rise minimal + 2° to +3°C. NO ADVERSE CONDITIONS NOTES. NO HAZARDOUS CONDITIONS. |

Figure 23. Test Flow and Description - 10,000 Ah Prismatic Cells (cont)

| SPECIMEN | TEST | CONDITION | RESULT |
|---|---|---|---|
| #4 | Low Temperature Storage | $-54^{\circ}$C/15 Days | Performance not affected after extended period of time at low temperature. |
| | Shock (Non-Op) | Transportation 100 g's, shock spectra | Electrical and structural integrity maintained during and after shock (3 axes). NO HAZARDOUS CONDITIONS. |
| #5 | Discharge to Zero Volts ($+25^{\circ}$C) | Discharge to C/O 36 Amps Discharge C/O to Zero at 18 Amps | Preliminary analysis indicates temp/pressure rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS. |
| | Vibration (Non-Op) (Discharge State) | Transportation 5 g's (peak) 5-50 Hz 2 g's (peak) 50-2000 Hz | Electrical and structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS. |
| | Shock (Non-Op) Discharge to Zero Voltage | Transportation 100 g's, shock spectra | Electrical and structural integrity maintained during and after shock (3 axes). NO HAZARDOUS CONDITIONS. |
| #6 | Temp/Venting Profile to C/O @ $+25^{\circ}$C | 70% of capacity @ 36 Amps, remaining 30% @ 18 Amps. No load condition after C/O @ $+150^{\circ}$F storage. | Preliminary analysis indicates temp/pressure rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS. |

Figure 23. Test Flow and Description - 10,000 Ah Prismatic Cells (cont)

The test under load lasted a total of 22.5 hours in which period the cell voltage changed from 3.67 V open circuit to 2.02 V immediately upon applying the load, then gradually increased to a maximum of 2.73 V one hour from the beginning of discharge before it started a gradual decline to a minimum of 1.05 V. The open circuit voltage was fully restored upon removal of the load at the end of the test.

The discharge current followed closely the change in voltage reaching a maximum of 203 A and remained slightly below this value for about 30 minutes before starting a gradual decline.

The case temperature reached a maximum of 51$^{\circ}$C approximately four hours after the load was applied. The internal pressure of the cell reached a maximum of 3.2 psi, coinciding in time with the temperature maximum. A slight negative pressure was developed inside the cell by the end of the test. No leakage, rupture, venting or explosion occurred during the test.

c. Post Discharge

The post discharge test was performed on one rectangular cell of 2000 Ah nominal capacity. A load twice the resistance of the nominal load was applied from cutoff at 3 V until the cell voltage reached zero. The purpose of the test was to reach a total exhaustion of lithium, so that the cell could be safely disassembled and disposed of.

The test was performed over the period of two weeks in which the cell voltage gradually declined to just a few millivolts, under load, and the discharge current became less than 1 mA. The cell's temperature followed the fluctuation of ambient temperature between 50 and 60$^{\circ}$F with no apparent relation to the state of discharge of the cell. The cell's internal pressure fluctuated with temperature fluctuation remaining just below the atmospheric pressure. The voltage of the cell has not recovered to higher than 0.12 V upon removal of the load.

d. Disposal

Upon the completion of the post discharge test, the cell was disassembled and the components were neutralized and left exposed to the neutralizing solution for a period of two weeks.

The deactivation well was covered with earth in a final disposal step following the neutralization period.

e. Vibration

One rectangular cell with the nominal capacity of 2000 Ah was subjected to the vibration test along all three axes (X, Y, and Z).

The cell was discharged for one hour at the nominal rate prior to the vibration test in each of the three directions and also for one hour following the completion of all vibration tests. The voltage, the discharge current, the internal pressure, and the case temperature were monitored during each of the four discharge periods. The discharge performance of the cell was found unaffected by the vibration that preceded the test in all discharge periods, including the final one. The cell voltage on discharge remained in the range of 3.35 to 3.45 V and recovered to the full open circuit voltage immediately upon removal of the load. No significant change in either the temperature or the pressure was observed during any of the discharge periods.

The vibration test was performed on cells in non-operating condition (at open circuit voltage). The frequency involved was applied as a sweep in a range of 5 Hz to 2000 Hz to 5 Hz at the sweep rate of 1 octave per minute for the duration of 16 minutes in each of the three directions. The open circuit voltage, the case temperature, and the cell's internal pressure were monitored for the duration of the vibration test. No change has been observed in any of the three parameters as a result of vibration.

f. Overdischarge

One cell of the nominal capacity of 2000 Ah was subjected to a full discharge equivalent to 50 percent of the capacity obtained on discharge. The cell voltage, the discharge current, the internal pressure, and the case temperature were monitored for the duration of discharge and overdischarge. The test lasted for a total of 380 hours, 252 hours of which the cell voltage remained positive. In the period of overdischarge, the voltage remained at a constant value of -1.7 V for almost the entire period.

The cell case temperature was $25 \pm 3^{o}C$ for the entire period of discharge. A steep increase in temperature to $35 \pm 2^{o}C$ coincided with the onset of overdischarge. After 80 hours of overdischarge, temperature settled at $30^{o}C$ where it remained for the rest of the overdischarge period.

The internal pressure remained under the atmosphere pressure (-0.5 psi) for the entire period of discharge. It climbed to 2 psi upon the onset of overdischarge. Its decline to the previous, slightly negative value coincided with the drop in the cell temperature from 35°C to 30°C, and it remained there for the rest of the overcharge period.

No leakage, venting, bursting, or explosion was observed during the overdischarge test.

g. Thermal Shock

The thermal shock test was performed on one prismatic cell of the nominal capacity of 2000 Ah in accordance with MIL-STD-810C, Method 503.1, except that the elevated temperature was $63 \pm 2^{o}C$ and the lower temperature was $-54 \pm 2^{o}C$. The cell was held in each of the two temperature chambers for four hours, and the cycle was repeated three times. The open circuit voltage, the cell's case temperature, and the internal pressure were monitored for the entire period of the thermal shock test. Following the thermal shock test the cell was allowed to equilibrate at room temperature before the one-hour discharge test was performed to determine the effect, if any, of the thermal shock on the performance characteristics of the cell. The same one-hour discharge test was applied to the cell prior to the thermal shock test for comparison.

The internal pressure of the cell varied between -7 psi and +7 psi, depending on whether the cell was going through the cold or hot part of the thermal shock cycle.

No change in the discharge performance of the cell was observed as a result of the thermal shock test. No leakage, rupture, venting, or explosion was observed during the thermal shock test.

h. Overheating

One prismatic cell was subjected to an overheating test in hot silicon oil, reaching a maximum of 121°C over a period of two hours and remaining at this temperature for an additional five hours. The open circuit voltage, the cell's case temperature, and the internal pressure were monitored throughout the test.

The open circuit voltage changed only in the range expected, corresponding to the increase in the temperature. It settled down at the initial full value, after cooling of the cell to room temperature following the test.

The cell's case temperature trailed closely the temperature of the oil in the bath.

The internal pressure of the cell climbed slowly to 6.3 psi during the oil heat-up period in the first hour of the test. At this pressure the cell vented into a scrubber, but the pressure continued to climb as the temperature of the bath increased, reaching a maximum of 23 psi 45 minutes after the oil bath temperature maximum was achieved. The pressure steadily declined over the last four hours of the test in spite of the constant temperature of the bath oil.

The scrubber temperature climbed, following the venting point, from 35°C to 105°C, when a slow steady cooling of the scrubber started, reaching 40°C at the end of the test.

The scrubber pressure continuously trailed the internal pressure of the cell, reaching a maximum of 17.3 psi at the maximum of the cell internal pressure of 23 psi. The difference between the two values remained at 6 psi for the entire period of the test, after the first venting, suggesting the proper functioning of the check valve between the cell and the scrubber. However, the check valve at the scrubber exit must have malfunctioned, since the high scrubber pressures were not expected.

Upon cooling to approximately 45°C following the test, the cell's internal pressure reached -12.6 psi, which was expected based on the fact that the cell lost some of its ingredients during the venting.

No leakage, rupture, or explosion occurred as a result of overheating.

i. Flammability

The flammability test was applied to one cell of the nominal capacity of 2000 Ah according to the MIL-STD-202E, Method 111A, by remotely applying a flame from torch for 15 seconds. The open circuit voltage, the cell's case temperature on the flame side, and the internal pressure were monitored during the 15-second test and 24 hours following the completion of the test.

No change was observed in either the cell's open circuit voltage or the internal pressure or the case temperature on the wall opposite the flame side. The case temperature on the flame side climbed to 98$^{o}$C in the 15 seconds of test and returned to the temperature of the opposite wall over a period of 35 minutes following the flame test.

No rupture, venting, leakage, or explosion was observed during the flammability test.

j. Temperature - Altitude

The temperature-altitude test was performed using one cell of nominal capacity of 2000 Ah. The cell was subjected to this test in a temperature-altitude chamber, according to MIL-STD-810C, Method 504. The chamber pressure was changed from ambient to that equivalent to 40,000 ft. altitude (2.7 psi) after the chamber temperature was changed from ambient to -65$^{o}$F. This temperature change was accomplished in one hour. These conditions were maintained for 50 hours, after which the pressure was then changed to ambient over one hour and the temperature was raised to 150$^{o}$F over a period of four hours. These conditions were also maintained for 50 hours thereafter. The chamber temperature was finally allowed to equilibrate with the ambient over a period of four hours.

Other than that expected, no change of the cell's open circuit voltage was observed as a result of the change in temperature. The performance characteristics of the cell were established through a one-hour discharge period following the test; they did not appear different from those established through the same type of discharge test prior to the test. The cell temperature and the scrubber temperature closely followed the temperature of the chamber. The cell pressure closely followed the pressure in the chamber at low temperature and showed a value of approximately +2 psi during the high temperature period following the low temperature test.

No venting, leakage, rupture, or explosion was observed on this cell during the test or thereafter.

## SECTION V

## SUMMARY

The work performed to date under this contract has demonstrated two significant achievements:

- o A safe lithium thionyl chloride battery can be designed and fabricated.
- o A primary energy source using lithium thionyl chloride technology is possible as shown by test for delivery of energy above 3.0 volts at $-40^{\circ}C$.

In addition to these achievements, preliminary quantification has been done on degradation and passivation phenomena.

Quantification of phenomena critical to cell performance, namely degradation and passivation, will continue through the remainder of the present contract.

Further technology improvement is recommended in the following areas for potential increased cell efficiency:

- o Electrolyte ionic conductivity, especially at low temperatures.
- o Increased surface activity of carbon cathodes.
- o Active and non-active material investigation for more efficient application to this technology.



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